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A Platform for Dynamic Process Simulation Demonstrated with a Peirce-Smith Converter Model

Master's Thesis for the degree of Master of Science in Technology submitted for inspection.

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Abstract of master's thesis

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Abstract

Chemical process simulation gives the initial data required for process design and engineering. Process simulation also provides a safe environment that can be used to train operators and optimize processes. Applications such as the HSC Chemistry® simulation platform can be used to model the complex behavior of chemical processes.

The target of this thesis is to develop a dynamic Peirce-Smith converter simulation model using the HSC Chemistry process simulation platform. This work consists of two parts. A dynamic calculation unit for pyrometallurgical applications is developed in the first part of the thesis. In the second part the new calculation unit is demonstrated with a Peirce-Smith converter model. In addition, a literature study is conducted in order to introduce the fundamental theories behind copper extraction and process simulation.

The design of the newly developed dynamic HSC unit is based on HSC's existing steady-state units, combined with new features essential for dynamic simulation. The new unit introduces tank layers that can be used to conserve mass and energy. Moreover, individual tanks can interact with the surrounding layers through separate operations.

The Peirce-Smith converter is modelled using separate tanks for slag, matte, blister and scrap metals. Chemical equilibrium is used to describe the boundary area between the different tanks. In addition, heat transfer and heat losses are described through model-specific formulas.

The new Peirce-Smith converter model is tested using data from a real-world smelter. The simulation results are compared to corresponding samples from the real-world smelter as well as previous Matlab and HSC models. The results suggest that the simulated composition of blister is relatively close to real-world samples. The model still requires development and tuning in order to accurately model slag.

Keywords Copper converting, Peirce-Smith Converter, Modelling, HSC Chemistry, HSC Sim, Simulation

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Sammandrag

Kemisk processimulering ger de grundläggande uppgifterna för processdesign och planering. Processimulering erbjuder även en trygg omgivning som kan användas för att utbilda operatörer samt optimera olika processer. Applikationer så som simuleringsplattformen HSC Chemistry® kan användas till att modellera olika kemiska processers beteende.

Målet med denna avhandling är att utveckla en dynamisk Peirce-Smith konverter simulerings modell med hjälp av simuleringsplattformen HSC Chemistry. Detta arbete består av två delar. En dynamisk beräkningsenhet för pyrometallurgiska ändamål är utvecklad i arbetets första del. I den andra delen demonstreras den nyutvecklade enheten med hjälp av en Peirce-Smith konverter modell. Dessutom utförs en litteratur studie som behandlar grunderna bakom koppar utvinning och process simulering.

Designen på den nyutvecklade dynamiska HSC enheten baserar sig på HSCs existerande statiska enheter tillsammans med en del nya koncept som är nödvändiga för dynamisk simulering. Den nya enheten introducerar lagringstankar, som kan användas till att lagra massa och energi. De Individuella lagringstankarna kan växelverka med omgivande lager genom olika operationer.

Peirce-Smith konvertern modelleras genom at använda olika lagringstankar för slag, skärsten, råkoppar och skrot metaller. Kemisk jämnvikt används till att beskriva området mellan de olika lagringstankarna. Värmeöverföring och värme förluster kan därtill beskrivas genom modell specifika formler.

Den nyutvecklade Peirce-Smith konverter modellen testas med hjälp av data från ett riktigt smältverk. Simuleringsresultaten jämförs med de motsvarande analyserna från den verkliga processen samt äldre Matlab och HSC modeller. Resultaten indikerar att de simulerade sammansättningarna för råkoppar är relativt nära de mätta värdena. Modellen måste dock ännu förbättras och kalibreras för att noggrant kunna modellera slag.

Nyckelord Koppar konvertering, Peirce-Smith konverter, Modellering, HSC Chemistry, HSC Sim, Simulering

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Robert Wahlström

Contents

Symbols

A	$[m^2]$	Area
E_a	$[J/mol]$	Activation energy
G	$[J]$	Gibbs free energy
H	$[J]$	Enthalpy
ΔH^0	$[W/mol]$	Released or absorbed energy by a reaction
ΔH_f^0	$[J/mol]$	Enthalpy of formation
K	[-]	Equilibrium constant of a reaction
Q	$[W]$	Heat transfer
R	$[J/(mol*K)]$	Ideal gas constant R= 8.3144598 J/(mol*K)
$R_{reaction}$	$[kg/s]$	Production rate
S	$[J/K]$	Entropy
T	$[K]$	Temperature
T_0	$[K]$	Starting Temperature
T_1	$[K]$	Final Temperature
U	$[J]$	Internal energy
V	$[m^3]$	Volume
$\dot{V}$	$[m^3/s]$	Volumetric flow
Z	[-]	Dimensionless factor
a,b	[-]	Stoichiometric relationships
c_p	$[J/(mol*K)]$	Specific heat capacity
d	$[m]$	Length
h	$[J/mol]$	Specific enthalpy
k	$[W/(m*K)]$	Thermal conductivity
m	$[kg]$	Mass
$\dot{m}$	$[kg/s]$	Mass flow
n	$[mol]$	Amount of substance
p	$[kPa]$	Pressure
r	$[mol/(m^3*s)]$	Rate of reaction
v	$[m^3/kg]$	Specific volume
x_i	[-]	Molality of substance
α, β	[-]	Reaction order
ε	[-]	Emissivity
σ	$[W*m^{-2}*K^{-4}]$	Stefan- Boltzmann constant σ=5.670373*10^{-8} Wm^{-2}K^{-4}
γ	[-]	Dimensionless activity coefficient
γ_T	$[1/K]$	Thermal expansion coefficient
μ	$[J/mol]$	Chemical potential of mixed substance
μ^0	$[J/mol]$	Chemical potential of pure substance

Abbreviations

BOHA	Boliden-Harjavalta smelter
DLL	Dynamic link library
FSF	Flash smelting furnace
HSC	HSC Chemistry software developed by Outotec
HSC Sim	Calculation module in HSC used for process simulation
MATLAB	Mathematical programming language
MVC	Model-View-Control software architectural pattern
.NET	Microsoft .NET framework.
PID	PID controller
PS Converter	Peirce-Smith converter
SIMP	System Integrated Metals Processing project
VB.NET	Programming language for the .NET framework

1. Introduction

The metal industry has undergone major changes in the last decade with decreasing raw material prices and lower margins. The new situation, along with the digital revolution, has led the industry to seek out new market areas in order to stay competitive. Pyrometallurgical technologies such as smelters and converters have been around for decades, but pyrometallurgical process simulation and optimization is still a relatively new area with plenty of growth potential.

Perhaps the safest and the easiest way to simulate a system is through a digital model. Process simulation is an imitation of a system and provides an excellent tool that can be used to predict, analyse and optimize the system. Process simulation models are typically based on fundamental theories that are described with mathematical formulas and equations.

Digital simulation models can be used to assist plant operators in complex applications where the process behaviour is well known. Technologies such as Peirce-Smith converters are widely used in the copper and nickel industry and can be modelled using chemistry, metallurgy and thermodynamics.

Peirce-Smith converters remove iron and sulphur from the matte, where the undesired elements are oxidized at high temperatures. The content is controlled by operators, who are responsible for adding and removing content to and from the converter. The converter should be operated under the right conditions in order to achieve the best results. Dynamic simulation can be used to estimate the ideal condition of the converter, and thus help the operator with important decisions.

Modelling Peirce-Smith converter operations in detail is often easier with a large parameter database as well as with a platform that is capable of solving complex equations. Simulation software such as HSC Chemistry® 9 can be used to model the complex behaviour and detailed equations required for PS converting.

The first objective of this thesis was to develop a general calculation unit for dynamic pyrometallurgical reactions in HSC Chemistry's Sim module. The developed calculation unit was designed as a foundation on which more detailed pyrometallurgical applications, such as PS converters, could be modelled. The second objective was to develop a more detailed dynamic copper PS converter model using the new calculation unit.

This thesis is divided into four sections. The fundamental theory of copper extraction and process modelling is introduced in chapter 2. Chapter 3 presents the developed pyrometallurgical calculation unit, whereas chapter 4 focuses on the detailed PS converter modelling. Finally, the results are presented in chapter 5.

2. Background

A basic understanding of the HSC Chemistry® simulation software, process simulation and copper converting is required in order to accurately model a Peirce-Smith converter. The necessary background information is introduced in this chapter.

2.1. HSC Chemistry®

Outotec Oyj is a Finnish company that was founded by Outokumpu Oyj in 2006. Outotec provides technologies and services for the metals and mineral processing industry. One of Outotec's products is HSC Chemistry® software. [1] [2]

The development of HSC Chemistry began in the mid-70s, and currently consists of 24 calculation modules that can solve a variety of different problems from thermodynamically equilibrium to chemical properties in different compounds. [2] [3]

This thesis was made with the HSC 9 simulation module commonly known as Sim 9. In addition, components from other modules in HSC were imported to Sim.

2.1.1. HSC Sim

HSC Sim is a flow sheet based simulation program that supports pyrometallurgical, hydrometallurgical, mineral and experimental processes. The reactions in pyrometallurgical processes are calculated according to a specific element distribution. Hydrometallurgical reactions are determined from given chemical reactions, and are typically based on pH and concentration. Mineral processing is designed to distribute materials according to a material's physical properties such as particle size, specific gravity or magnetic properties. HSC Sim was primarily developed for the mining and mineral industry, but the software can be applied to other areas as well. [3, pp. 24-25]

The primary use of HSC Sim is to model mass and energy flows in steady state and dynamic processes. The software can calculate the chemical properties of material flows and reactions. Energy efficiency, environmental impacts, and sustainable effects of the process can be determined with HSC Sim. Dynamic simulation modules are currently only for Outotec's internal use, with a public release scheduled for the end of 2017. One of the aims of this thesis was to define and develop a dynamic pyrometallurgical calculation unit for HSC's unit library. [3, pp. 24-25]

2.1.2. HSC Equilibrium module

The HSC Equilibrium module solves the chemical equilibrium by minimizing Gibbs free energy. The module can solve the chemical equilibrium as a range of two independent variables, such as temperature and pressure, in order to visualize the effect of the given variables. Activity coefficients for ideal mixtures can be defined as fixed or as a function of temperature or composition. [3, p. 7]

2.1.3. HSC Database

HSC Chemistry's database consists of 28 000 compounds from different literature sources. The database contains properties such as c_p coefficients, formation enthalpy, formation entropy, solubility and molar weight. Properties such as enthalpy and entropy are calculated from the database constants. One of the reasons that this thesis could even be implemented was because of the large number of entries in the HSC database. In this thesis the HSC database was primarily accessed for the purpose of solving thermal equilibrium problems. [3, p. 21]

2.2. Copper extraction

Around 80 % of the world's copper production originates from sulphide ores, such as chalcopyrite ($CuFeS_2$) and chalcocite (Cu_2S). The copper concentrations in sulphide ores are typically around 0.5-2 %. Cu-Fe-S minerals are not easily dissolved by aqueous solutions, which is why most copper extraction processes are pyrometallurgical. Copper is typically extracted in four steps: mineral processing, smelting, converting and refining. A flow sheet of a modern day copper smelter is illustrated in Figure 1. [4, pp. 1-2]

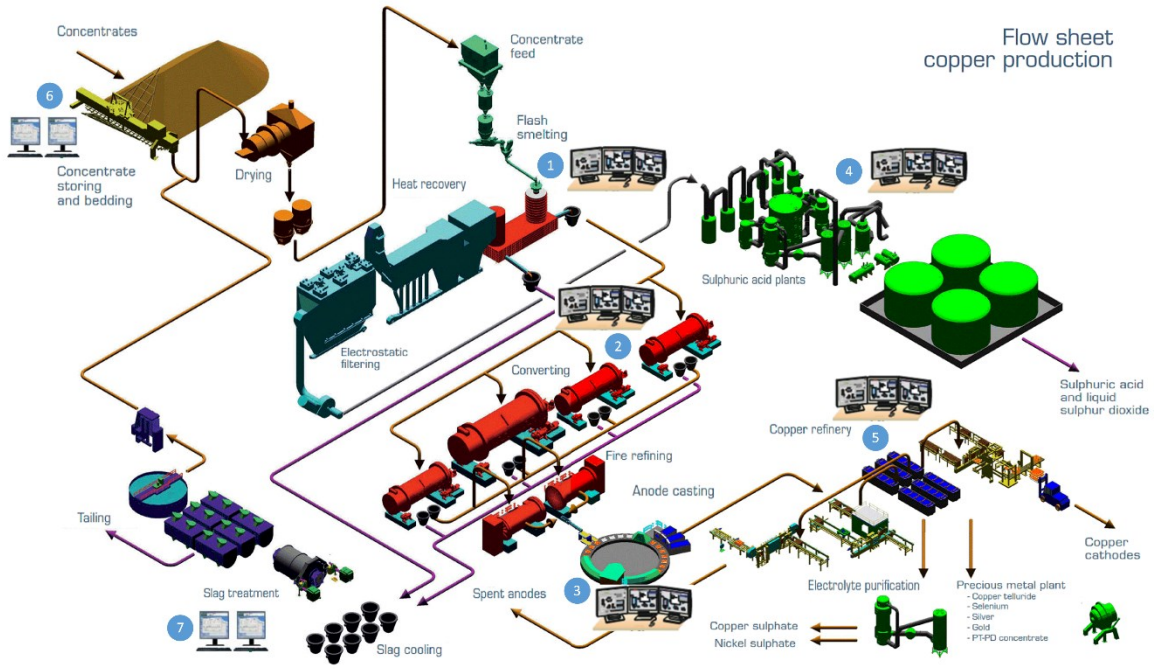


Figure 1. A typical copper smelter flow sheet. The copper undergoes feed mixture preparation (point 6), flash smelting (1), converting (2), anode casting (3) and refining (5). Slag treatment (7) and SO_2 treatment (4) are included in the flow sheet. [5]

Refined copper typically has a concentration of around 99.95 % Cu. The focus of this thesis was to implement a dynamic copper converter model. Preceding and subsequent process steps such as concentration, smelting and refining will therefore only be discussed briefly.

2.2.1. Minerals processing

Most copper ores mined today contain a vast portion of unwanted rock or gangue minerals of little value. Heating and melting the large amount of waste rock would require an excessive amount of energy. Fortunately, the valuable Cu-Fe-S minerals can be separated from the waste minerals by means of physical properties, thus forming a high Cu-Fe-S concentrate for further processing. [4, pp. 4 & 31-36]

The first stage of separating the waste rock from the valuable minerals is by crushing and grinding the minerals into small (~50 μm) particles, which liberates the Cu-Fe-S minerals into individual solid particle phases. [4, p. 4]

Copper, iron and sulphur are extracted from the crushed ore through froth flotation. The valuable minerals are attached to air bubbles that rise to the surface and hence become separated from the rest of the ore. The copper concentrate after froth floatation is roughly 30 %. [4, pp. 4 & 51-56]

2.2.2. Smelting

The Cu-Fe-S concentrate from froth flotation is typically smelted into molten matte. There are multiple techniques used for smelting, with Outotec's flash smelting furnace (FSF) being the most common [4, p. 89].

Smelting entails heating, oxidizing and fluxing the concentrate at high temperatures (1250 °C). Some parts of the iron are oxidized and form slag, which is poured out of the smelter. The products of smelting consist of molten matte, molten iron-silicate slag and off-gases containing sulphur dioxide (SO_2). The molten matte is sent to converting whereas the slag is recycled for further extraction of copper. [4, pp. 4-5]

2.2.3. Converting

Converting is a method to treat the sulphides in matte to produce blister copper and slag. The iron and the sulphur in matte are oxidized with oxygen-enriched air. Copper converting is mostly done in horizontal Peirce-Smith converters that convert Cu-Fe-S containing matte into blister, which is 99 % metallic copper. The converting process occurs between the smelting and the fire refining processes. [4, pp. 5-7] [6, p. 6]

2.2.3.1. Chemistry of converting

Converting is a batch process in which matte reacts with air and silica to eventually form off-gases, slag and blister. The converting process is exothermal and must be monitored by an operator. The overall process can be described by reaction (1). [4, p. 127]

$$\underset{Matte}{\begin{Bmatrix} Fes \\ Cu_2S \end{Bmatrix}} + \underset{Air}{O_2} + \underset{Silica}{SiO_2} \rightarrow \underset{Copper}{Cu} + \underset{Slag}{\begin{Bmatrix} 2FeO*SiO_2 \\ Fe_3O_4 \end{Bmatrix}} + \underset{Off-gas}{SO_2} \quad (1)$$

Copper converting can overall be divided into two stages. The first stage is the formation of slag, also known as the slag blow, where iron sulphide reacts with air to form sulphur dioxide

and iron oxides. The second stage is called copper making, where copper sulphide is oxidized to form copper and sulphur dioxide. [4, pp. 127-134]

Slag is formed from the Fe in the matte and the SiO_2 in the flux. The main oxidation reactions during the slag blow are (2), (3) and (4). [4, p. 127]

$$FeS + 1.5O_2 \rightarrow FeO + SO_2 \quad (2)$$
$$3FeS + 5O_2 \rightarrow Fe_3O_4 + 3SO_2 \quad (3)$$
$$2FeO + SiO_2 = 2FeO * SiO_2 \quad (4)$$

The composition of slag is controlled by additional flux. The melting points of wüstite (FeO) and magnetite (Fe_3O_4) are a lot higher than that of the converter, so silica (SiO_2) is added to lower the melting point of the slag. Silica and iron oxide compounds form fayalite ($2FeO*SiO_2$), which has a much lower melting point than the individual iron oxide compounds. Maintaining the operating temperature is important in order for slag to sufficiently capture the correct elements as well as for controlling the viscosity. [4, p. 127] [6, p. 15] [7]

The slag blow is finished when the matte contains about 0-1 % of iron. The remaining matte, or 'white metal' as it is termed, mainly consists of copper sulphides at approximately 1200 °C [4, p. 128].

The slag blow is followed by copper making in what is called the copper blow. The copper making is mainly carried out in reactions (5) and (6). [4, p. 129]

$$Cu_2S + \frac{3}{2}O_2 \rightarrow Cu_2O + SO_2 \quad (5)$$
$$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2 \quad (6)$$

It is also possible to convert copper directly according to reaction (7). [4, pp. 129-131]

$$Cu_2S + O_2 \rightarrow 2Cu + SO_2 \quad (7)$$

The formation of blister (which primarily consists of metallic copper) is carried out in three sequential steps. In the first step, oxygen is blown into the system where it removes sulphur from the white metal. The sulphur grade is lowered, but the reaction will not form any metallic copper. [4, p. 131]

The second step begins when the sulphur content in white metal is reduced to about 19.6 %. Blasting additional air into the system will form dense metallic copper that sinks to the bottom of the converter, thus forming the blister phase. The reaction will continue to produce blister at the expense of matte as more air is blown into the system. The converter will contain both matte and blister as long as the compositions of both phases are in the immiscibility range. [4, pp. 131-134]

The third step begins when the converter contains so little sulphur that the matte phase disappears, and only blister remains. The blister will at this point contain about 1 % of sulphur, which is removed by further blasting air into the converter. The air blast stops when

the sulphur has been removed, as additional air would over-oxidize the copper into copper oxide (Cu_2O). [4, p. 134]

2.2.3.2. Slag, Matte and Blister

The phases involved in converting are slag, matte and blister. The remaining high copper matte after the slag blow is referred to as white metal, as mentioned above. Typical element analyses for the respective phases are shown in Table 1.

Table 1. Typical element analysis for matte, white metal, blister and slag according to the literature. [4, p. 135] [8, p. 140]

	Matte	*White Metal*	*Blister*	*Slag*
Cu	45-75	79	~99	4-8
Fe	3-30	~1	0.001-0.3	35-50
S	20-23	~20	0.001-0.3	
O	1-3	<1	0.1-0.8	
As	0-0.5		0-0.2	
Bi	0-0.1		0-0.03	
Pb	0-1		0-0.5	
Sb	0-0.5		0-0.1	
Zn	0-1		0	
Au	0-0.003		0-0.004	
Ag	0.03		0-0.5	
Al_2O_3				0-5
CaO				0-5
ZnO				0-5
SiO_2				15-30

Molten matte has a relatively low viscosity compared to slag. The melting point of matte depends on the copper concentrate, and is usually between 940-1100 °C. Matte primarily consists of copper sulphides (Cu_2S) and iron sulphides (FeS). The iron content in the matte degrades during the slag blowing process, thus increasing the copper content in matte. [8, p. 84]

Slag is a by-product of the metal extraction process that primarily consists of molten iron oxides, but also contains elemental metals and metal sulphides such as FeS and Cu_2S.

The molecule structure of oxides in slag can be divided into acid, basic and neutral. High concentrations of acidic oxides (SiO_2, Al_2O_3) impart high viscosity to the slag and make it difficult to process. Basic oxides will have the opposite effect and can, to a certain point, lower the melting point of the slag. The slag used in copper making typically contains a small fraction of basic oxides. Neutral oxides (FeO, Cu_2O) tend to lower the slag's melting point and viscosity. [4, p. 74]

The melting point of most slags is around 1200 °C, which is slightly higher than that of matte. As a consequence, the choice of operating temperature is primarily driven by the composition of the slag. The heat balance and the operating temperature can be controlled by adding flux to the converter. [4, p. 81]

The density of slag is around 2.8-3.8 t/m^3 [9]. The corresponding density of Cu_2S-FeS matte is between 4-5.3 t/m^3, which causes the slag to rise to the top [4, p. 82]. The heat radiation from slag will form a thin solid crust on the top.

Removed slag can be recycled back through mills and concentrators in order to recover the remaining copper. Iron can be further recovered from the iron oxides in slag using other pyrometallurgical methods.

2.2.3.3. Industrial Peirce-Smith converters

Nowadays most copper converting is done in PS converters [10, p. 8]. The length of an industrial-sized PS converter is typically 2-2.5 times its diameter. There is a current trend towards larger vessels that are roughly 4.5 m in diameter and 13 m in length. Figure 2 shows a PS converter at the Harjavalta smelter in Finland. [6, p. 21]

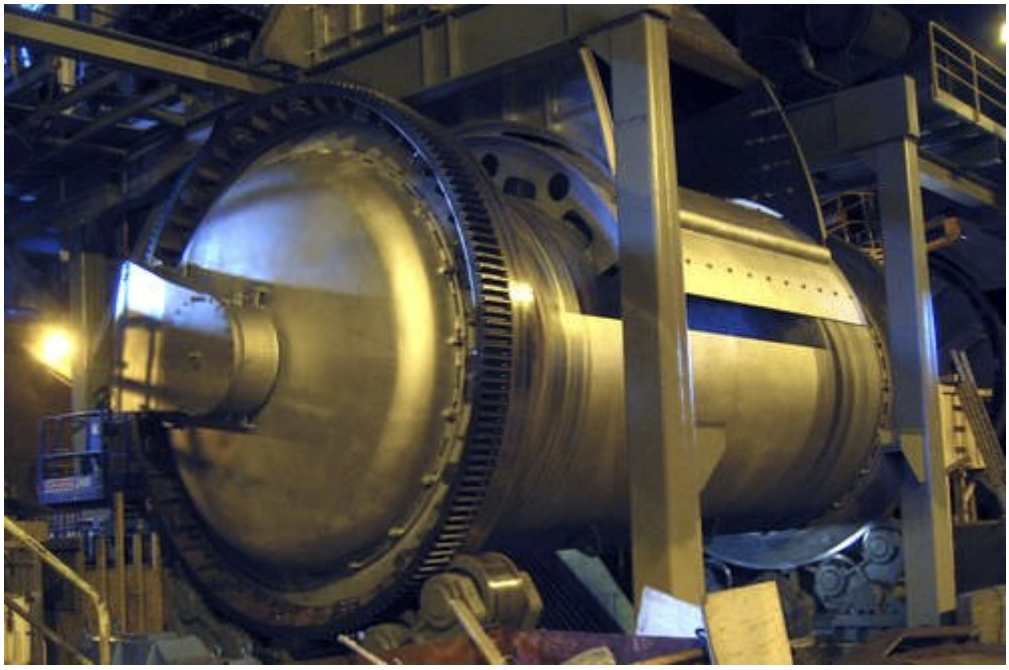


Figure 2. Industrial Peirce-Smith converter at the Harjavalta smelter. [11]

The converter shell is usually made of 0.05 m thick steel lined with up to 0.5 m thick brick made of 60 wt% magnesia (MgO), 20 wt% chromium oxide (C_2O_3), 8 wt% alumina (Al_2O_3), 7 wt% wüstite (FeO), and small amounts of silica (SiO_2), calcium oxide (CaO) and active metals. [4, p. 134] [6, p. 22]

Air is blown into the converter through tuyères (see Figure 3) that are 5 cm in diameter. The tuyères are placed 15-40 cm apart and can deliver between 80 and 1000 Nm^3/min of air. The air enters the matte 0.5-1 m below the surface. A well-functioning converter retains 90-95 % of the oxygen, while the remaining oxygen is removed with the off-gas. The SO_2 in the off-gases can be used to produce sulphuric acid. Enriched air can be used to minimize the heat spill with the off-gas as well as increasing the viability of producing sulphuric acid from the sulphur dioxide in the off-gas. About half of the operating PS converters enrich the air with oxygen. [6, pp. 21-23]

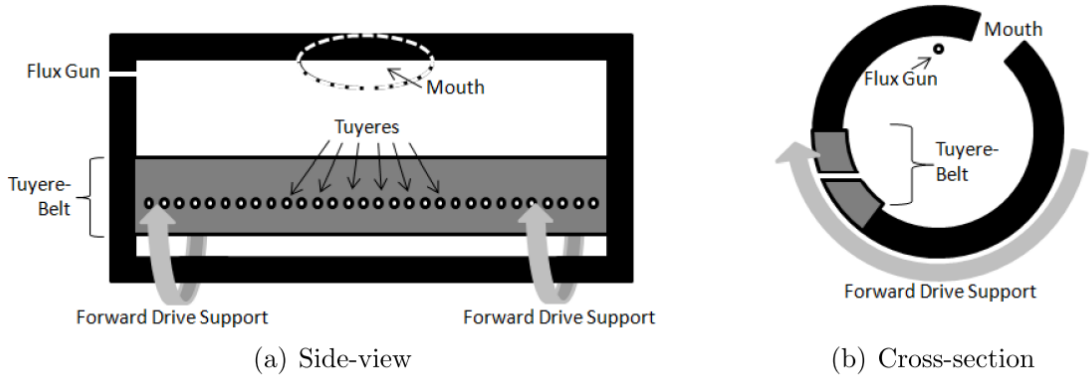


Figure 3. Side-view (a) and cross-section view (b) of a typical Peirce-Smith converter. [6, p. 20]

Approximately 200 tonnes of 60 Cu % matte are converted in 6-12 hour cycles. The number of converters for a single smelter depends on the overall smelting capacity, but is often between two and five. [4, p. 134] [6, p. 21]

The PS converter can rotate along its central axis. The mouth of the converter is in forward position at the beginning of a cycle, so that the matte can be poured into the converter. The converter is rotated back to the upright position once matte has been added in order to avoid spills and to collect off-gases. Silica is added either through flux guns or through chunters, and will together with iron and oxygen form slag. The accumulated slag is poured out by rotating the converter back to its forward position. The removed slag is replaced with matte as the converter is partially rotated backwards. The converter is then moved back to the upright position and the process is repeated until most of the iron has been removed. The converter is in upright position when the sulphur is removed by air blast during copper blow. The converter is again rotated to the forward position when secondary feeds are added to the converter. The secondary feed prevents the converter from overheating, and may consist of scrap metals, reverts or flue gas dusts. The remaining slag and blister products are finally discharged from the converter at the end of the cycle. [6, pp. 14-21 & 40]

2.2.4. Refining

The converted 99 % Cu blister copper contains small fractions of impurities that are removed through fire refining in anode furnaces. The blister copper contains about 0.02 % sulphur and 0.3 % oxygen. The sulphur is oxidized into sulphur dioxide whereas the oxygen is reduced with help of hydrocarbon fuels (C_nH_m) that produce carbon oxides (CO_x) and water (H_2O). The name “anode furnace” comes from the end product, which is sufficiently pure to be cast into anodes (~99.5 % Cu). The anodes are afterwards subjected to electrorefining, which produces a 99.95 % Cu cathode. [4, p. 237] [6, p. 11]

2.3. Thermodynamics and chemical reactions in process modelling

The goal of process simulation is to provide information about the process, which is used to manufacture products at the lowest cost possible. Generally, the entire process consists of multiple sub-processes in which the product is refined. [12, p. 1] [13]

It is advisable to break down the model into smaller sub-phases, thus making it easier to validate whether the process is correctly dimensioned and economically feasible. Under-dimensioning will result in the process not reaching its requirements whereas over-dimensioning will increase the production cost. [12, p. 2] [13]

Process simulation is based on the fact that behind every action there is a fundamental theory. Chemical processes can, for instance, be modelled using thermodynamic equilibrium. A system is said to be in thermodynamic equilibrium when it satisfies the conditions of thermal, mechanical and chemical equilibrium. Thermal equilibrium is reached when the temperature is uniform over the entire system. A system is said to be in mechanical equilibrium when there are no unbalanced forces and when the pressure throughout the system remains constant. A system is in chemical equilibrium when the chemical composition remains constant over time. Thermodynamic equilibrium can be used as a theoretical reference state which the system approaches over time. [14]

2.3.1. Mass balance

The mass balance is typically very important in process simulation. In general, the mass balance of any component can be modelled with equation (8). [15]

$$\begin{pmatrix} Rate\ Of \\ accumilation \\ of\ mass \\ component\ i \\ in\ the\ system \end{pmatrix} = \begin{pmatrix} Mass\ flow \\ of \\ component\ i \\ into \\ the\ system \end{pmatrix} - \begin{pmatrix} Mass\ flow \\ of \\ component\ i \\ out\ of \\ the\ system \end{pmatrix} + \begin{pmatrix} Rate\ of \\ production \\ of \\ component\ i\ by \\ the\ reaction \end{pmatrix} \quad (8)$$

Equation (8) can be described using the corresponding formula

$$\frac{dm}{dt} = \dot{m}_{in} - \dot{m}_{out} + R_{reaction} \quad (9)$$

where $\frac{dm}{dt}$ is the accumulated mass in the system, $\dot{m}_{in}$ the input flow, $\dot{m}_{out}$ the output flow, and $R_{reaction}$ the production rate. For steady-state models, the rate of accumulation of mass in the system is always zero. [15, p. 19] [16, p. 57]

2.3.2. Reaction kinetics

Reaction kinetics describes the rate at which reactions occur in a system. It is important in dynamic process modelling to be aware of the reaction rates and which factors it controls. Slow reactions in particular need to be modelled carefully as they tend to have a great impact on the result. [12]

The rate of the reaction for component *i* can be defined as

$$r_i = \frac{1}{V}\frac{dn_i}{dt} \quad (10)$$

where *r* is the rate of the reaction, *V* the volume, and *n* the amount of the solute. [17, p. 4]

The reactants and products are often related by a stoichiometric equation that represents a molar relationship

$$aA + bB \rightarrow cC + dD \tag{11}$$

where [$a \ldots d$] are the stoichiometric relationships between the components in the reaction.

The individual reaction coefficients can be expressed via their stoichiometric relationship according to (12). [17]

$$r_A = r_B \frac{a}{b} \tag{12}$$

The reaction rate is usually described as a dependency of temperature and concentration. The rate equation can be expressed as

$$r_i = k_0 f_1(T) f_2([C_i \ldots C_{i+n}]) \tag{13}$$

where k_o is the reaction constant, $f_1(T)$ the reaction's temperature dependency, and $f_2([C_i \ldots C_{i+n}])$ the reaction's concentration dependency. [17]

The temperature dependency can be described using the Arrhenius law,

$$f_1(T) = Ze^{-E_a/RT} \tag{14}$$

where Z is the pre-exponential factor, E_a the activation energy, R the ideal gas constant and T the active temperature in Kelvin. Arrhenius law is a good method to approximate a reaction's temperature dependency both according to the collision and the transition-state theories. [17, p. 28]

The concentration dependency is usually found experimentally and is a function of one or more concentrations. It has the general form

$$f_2([C_i \ldots C_{i+n}]) = C_i^{\alpha} * \ldots * C_{i+m}^{\beta} \tag{15}$$

where C is the concentration of component i, and α and β are the order of reaction in respect to the corresponding concentration. The rate order is determined from observations. Partial pressure is sometimes used in place of concentration

$$f_2([p_i \ldots p_{i+n}]) = p_i^{\alpha} * \ldots * p_{i+m}^{\beta} \tag{16}$$

where p_i stands for the partial pressure of compound i. [17]

2.3.3. Thermodynamics in process simulation

Thermodynamics can be applied to model the heat balance and the reaction kinetics based on the theoretical chemical equilibrium. [12, p. 2]

The heat capacity in HSC is estimated according to the Kelley equation

$$c_p(T) = A + B * 10^{-3} * T + C * 10^5 * T^{-2} + D * 10^{-6} * T^2 + E * 10^8 * T^{-3} + F * 10^{-9} * T^3 \quad (17)$$

where coefficients *A, B, C, D, E* and *F* are experimental coefficients. [13, p. 5]

The enthalpy under a given set of circumstances can be expressed as

$$h(T,p) = \Delta H_f^0(T_0) + \int_{T_0}^{T} c_p(T,p_0)\, dT + \int_{p_0}^{p} v(T,p)\big(1 - T * \gamma_T(T,p)\big)\, dp \quad (18)$$

where T_0 and p_0 stand for temperature and pressure in the reference state, ΔH_f^0 the enthalpy of formation, v the specific volume, γ the thermal expansion coefficient and c_p the specific heat capacity. The last pressure integral is usually insignificantly small under normal operating conditions, and the specific enthalpy is therefore often simplified to only include temperature [18, p. 58]. 25 °C and 1 bar are used in HSC as the reference state. [13, p. 5] [19, pp. 29-33 & 61]

2.3.4. Heat balance and heat transfer

The first law of thermodynamics states that energy can neither be created nor destroyed. This means that the transferred energy for a closed system can, regardless of the path, be determined from the initial state and the final state. [19]

An energy balance means that the algebraic sum of energy accumulation, energy transfer and energy released/absorbed by the system is zero. The energy balance is generally expressed as

$$\frac{dU}{dt} = \Delta H^0 * n + \sum_i Q_i \quad (19)$$

where U is the system's internal energy, ΔH^0 the energy released/absorbed by the system, and Q the energy exchange with the surroundings. The energy accumulation in steady-state conditions is always equal to zero. [19]

Chemical reactions absorb or release energy depending on the reactants. Exothermic reactions release energy whereas endothermic reactions absorb energy. The specific enthalpy is used to determine the absorbed or released energy of the chemical reaction

$$\Delta H^0_{recation} = \sum_j (n_j * h_j(T_j, p_j)) - \sum_i (n_i * h_i(T_i, p_i)) \quad (20)$$

where $\Delta H^0_{recation}$ is the enthalpy absorbed or released in the reaction, n the compound amount, h the specific enthalpy, and i and j are the compound amounts before and after the reaction. [19, pp. 42-45]

Energy can be transferred as heat, mechanical and electrical work. In chemical reactions, energy is typically transferred as heat between the system and the surroundings. Heat can be transferred through conduction, convection and radiation. The direction of heat transfer is always from a hot reservoir to a cold reservoir, as stated by the second law of thermodynamics [4, p. 88]. In the absence of external heat sources, temperature difference decays over time as the system approaches thermal equilibrium. [20]

Thermal conduction (in many cases referred to as diffusion) is the transfer of heat from molecular collision and movement on a microscopic scale. Heat is directly transmitted through a medium that separates two regions of different temperature. In thermal conduction, heat is transferred without moving the actual material. Thermal conduction can be described as

$$Q = \frac{kA\Delta T}{d} \tag{21}$$

where k is thermal conductivity, A the surface area, d the thickness and ΔT the temperature difference between the two regions. [16, p. 242]

Convective heat transfer is the transfer of heat by mass motion of fluids. Convection is often regarded as a distinct method of heat transfer, but is in fact a combination of advection (fluid flow) and conduction. Convection can either be forced or natural. Forced conduction creates an artificial convection current using an external force such as fans or pumps. Natural convection is caused by temperature and density variation in the fluid. Convection is usually the dominant form of heat transfer in liquids and gases. [20]

Thermal radiation is the transfer of energy by means of electromagnetic waves. Thermal radiation can, unlike thermal conduction, occur in a vacuum. The characteristics of thermal radiation depend on the surface properties and temperatures of both the transmitting and the receiving regions. Stefan-Boltzmann's law can be used to describe the radiation heat loss from a region in terms of its temperature

$$P = A * \varepsilon * \sigma * T^4 \tag{22}$$

where T is the surface temperature, ε the emissivity which is characterised as $\varepsilon<1$ and σ the Stefan-Boltzmann constant. [20]

2.3.5. Chemical equilibrium

Chemical equilibrium can be used to describe the theoretical composition of a compound. Chemical equilibrium can be solved from minimizing the Gibbs free energy. The equation for Gibbs free energy is

$$G = H - TS \tag{23}$$

where G is the Gibbs free energy, H the systems enthalpy, S the systems entropy and T the temperature in Kelvin. [19, pp. 51-52]

Gibbs free energy can further be described with

$$G(T, p, n_i, \dots, n_m) = \sum_{i=1}^{m} n_i \frac{\partial G}{\partial n_i} = \sum_{i=1}^{m} n_i \mu_i \tag{24}$$

where n_i stands for the mol and μ_i for the chemical potential in substance *i.* Solving the derivate will result in equation (25).

$$dG = \sum_{i=1}^{m} \mu_i dn_i = \mu_1 dn_1 + \cdots + \mu_m dn_m = 0 \tag{25}$$

Equation (25) can be used to solve the chemical equilibrium after replacing [$dn_i \dots dn_m$] with the corresponding stoichiometric reaction constants discussed in section 2.3.2. Solving the chemical equilibrium thus requires solving the common variable, as the chemical potential only depends on the active state. The chemical potential for pure substances is defined as

$$\mu_i^0 = \frac{\partial G}{\partial n_i} = \frac{\partial H}{\partial n_i} - T \frac{\partial S}{\partial n_i} \tag{26}$$

where n_i stands for the mol of substance *i.* The chemical potential describes the effect of a small change in composition in Gibbs free energy. [19, pp. 52-55]

Not all substances are pure, which means that the molality must be taken into consideration. The chemical potential for an ideal solution is

$$\mu_i = \mu_i^0 + RT * \ln(x_i) \tag{27}$$

where μ_i^0 is the chemical potential of the pure substance, R the ideal gas constant, T the active temperature and x_i the molality of substance i. [19, pp. 113-115]

Non-ideal solutions are calculated by accounting for the so-called activity coefficient

$$\mu_i = \mu_i^0 + RT * \ln(\gamma_i * x_i) \tag{28}$$

where γ_i is a dimensionless activity coefficient. [19, pp. 113-115]

A system can contain multiple phases. Combining the Gibbs free energy equation (24) and the chemical potential equation (28) gives (29).

$$G = \sum_{k} \sum_{i} (\mu_i^0 + RT * \ln(\gamma_i * x_i) * n_i) \tag{29}$$

Gibbs free energy is the sum of the Gibbs free energy in compound i for all phases in k. [13, pp. 5-7]

Chemical equilibrium can also be solved from the equilibrium constant. The equilibrium constant is defined as

$$K \equiv \frac{(\gamma_C * x_C)^c * \ldots * (\gamma_D * x_D)^d}{(\gamma_A * x_A)^a * \ldots * (\gamma_B * x_B)^b} \quad (30)$$

where K is the equilibrium constant for reaction $aA+\ldots+bB=cC+\ldots+dD$. [19, pp. 86-89]

The equilibrium constant can be solved from

$$\Delta G = -RTln(K) \quad (31)$$

where G is the Gibbs energy, R the ideal gas constant and T the active temperature in Kelvin. [19, pp. 86-89]

2.4. Modelling and simulation

Computer simulation is defined as the process of creating a digital imitation of a real world system, which behaves according to a certain rule and/or a mathematical theory. Many processes include unsystematic behaviour and cannot always be modelled exactly according to the corresponding real-world process. Computer simulation is used to give an overview of the direction in which the process is heading. The ultimate goal of computer simulation is to predict the future behaviour of the system and identify those factors which control it. [21]

Building a process model involves many important decisions regarding for example the structure and its variables. Other important decisions are whether a system is steady-state or dynamic, and continuous or discrete. The approach should be chosen wisely, as it will have a significant impact on the final simulation model. [21]

2.4.1. Steady state simulation

Steady state models are independent of time and are therefore used in systems that have reached a constant state. Steady state also means that neither mass nor energy is accumulated in the system. [21]

Steady state can be solved with both algebraic equations and by iterating the model multiple times. Steady-state models are in general easier to solve compared to dynamic models, as the time variable in dynamic models will often lead to complex differential equations. Steady-state simulations can also be used to model continuous processes that approach a steady state. [12] [21]

2.4.2. Dynamic simulation

Dynamic models are a lot more complex than steady-state models. Dynamic models hardly remain constant, but may slowly approach equilibrium. The mass and element balances must also take accumulated content into account. Dynamic simulation is used for batch processes and can also be used to model continuous processes that approach a steady state. [12]

Dynamic simulations are able to model situations in which either the operator or the automation system perform changes on one or multiple variables. A good example would be the modelling of start-ups and shutdowns where several adjustments are performed simultaneously. [12, pp. 18-20]

Variable adjustments may be performed according to a pre-defined time schedule or according to a specific event. One way to implement event-based models is by using logical operators. Time-scheduled models can be regarded as event-based models in which the logical operators perform changes according to the time variable. Event-based and time-based adjustments can co-exist in dynamic models. [12, pp. 18-20]

A large-scale automation system may contain thousands of adjustable parameters, which means that performance is a critical factor in dynamic simulation. Performance issues are one of the greatest disadvantages of dynamic models compared to steady-state models. Steady-state models only need to solve the equilibrium state once whereas dynamic models must simulate the process path from start to end. [12, pp. 18-20]

A numeric approach in dynamic simulation is often better than an analytical approach, as numeric approaches are generally faster, at the expense of accuracy. The accuracy of the numeric approach is determined by the calculation time step. Smaller time steps will increase the accuracy but will also require more computation and will therefore make the model slower. [12, pp. 18-20]

2.4.3. Continuous and discrete processes

There are two alternative frameworks that can be used for time modelling. Continuous- time models process the variables as a smooth function with an infinite number of states, while discrete-time models process the variable as fixed over a certain time interval with a limited number of states. Steady-state models are independent of time, which means that the approach is insignificant. Dynamic models however depend on time, thus making the approach important. [22, pp. 1-2]

Continuous models are in general better at analysing processes in which feedback significantly affects the behaviour, whereas discrete models are better at analysing the behaviour of linear processes and modelling discrete changes. Discrete models can typically run significantly faster than the corresponding continuous model because of the finite number of states. [22, pp. 1-2]

2.4.4. Modelling

A good guideline for modelling is to split the system into smaller sub-systems. Small sub-systems often give a better overview, are easier to analyse and make the components reusable in similar processes elsewhere. Small sub-systems also make testing and debugging significantly easier as it provides a simple tool to visualize the calculation steps.

Robinson [21, p. 68] specifies that the aim should be to “keep the model as simple as possible to meet the objectives of the simulation”. According to the Pareto principle “the few (20 %) is usually responsible for the many (80 %)” [23]. This means that that after a small (20 %) complexity level, the model will gain very little accuracy.

According to Robinson [21, p. 53] the milestones of process modelling are the following:

- Develop and understand of the problem
- Determine the modelling objective
- Design the conceptual model: inputs, outputs and model content
- Collect and analyses the data required to develop the model

Robinson [21, p. 54] defines the key issues of process modelling as:

- Obtaining accurate results
- Searching the solution space
- Testing the robustness of the solution (sensitivity analysis)

Simpler models can be validated by comparing the model to a set of scientific laws. Large-scale application models, however, can be quite complex and should be evaluated by other means. A more reliable way to validate models is by comparing model data with actual measurement data. [21]

Searching the solution space can, especially for large models, be time-consuming. Experiments are usually conducted in order to find solutions to the problem. Experimenting is a process of "what-if" thinking, where the consequences of small parameter adjustments are analysed for the next calculation round. The "what-if" modelling process is illustrated in Figure 4. [21, p. 53]

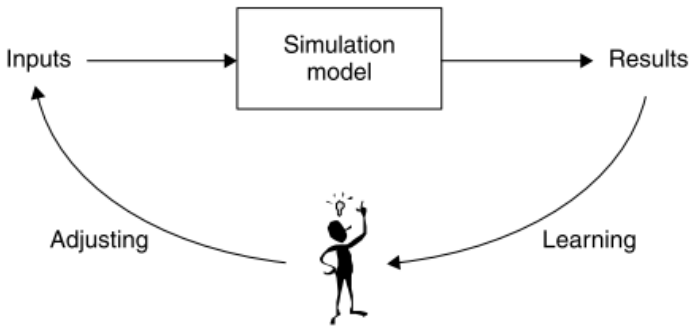


Figure 4. The key steps in "what-if" process modelling. [21, p. 53]

Some, but not all models, are required to exchange data with a real-time system. These kinds of models can, for example, be part of an automation system, which in real time predicts the end state so the process variables can be adjusted accordingly. The model and the data sensors are often linked through a data interface.

2.4.5. Advantages and disadvantages with simulation

One advantage of process simulation is that it allows testing of new ideas without interrupting an ongoing operation. Simulation provides insight in which variables control the system without the need for carrying out any practical experiments. Computer-based simulation provides a sufficient tool to analyse and repair bottlenecks. [21]

Simulation models can be used to experiment with systems that have not been implemented, systems that require expensive lab equipment or systems that are too dangerous to test with the available equipment. [21]

It is likely that experimenting with a real-time system will be costly. It is expensive to interrupt an ongoing process for testing purposes. Some systems must even be powered off in order to be altered. Computer-based simulation provides an excellent tool for making changes at only the cost it takes to alter the model and without any interruptions in the real-world system. [21]

Simulation models can also be used for training process operators. It provides a safe environment with realistic process behaviour. New production plants can be tested in advance in order to optimize the automation system. Process simulation provides an excellent tool for system optimization. [21]

The disadvantages of process simulation include cost, time consumption, data acquisition, requirement of expertise and excessive confidence in the model. Software licenses cost money and might require investments in training or consultants. Building models is a time-consuming process and the benefits are not immediate. Simulations are often calibrated according to the available data, which might not always be reliable or may require processing. Analysing the data and building the model requires a good deal of knowledge about the process. Simulation models should always be approached from a critical point of view as the underlying model might contain assumptions or simplifications. The user might have excessive confidence in the simulation model and may therefore not identify hazardous situations. [21]

2.5. Modelling and simulation in HSC Sim

HSC Sim supports two different types of models: Excel models and dynamic link library (DLL) models.

2.5.1. Model architecture in HSC Sim

Simulation and calculation for most of HSC's steady-state pyro and hydro units are done with Excel spreadsheets, where values are calculated using Excel formulas. The cell references in the HSC Excel models are automatically generated using macros. It is convenient to use Excel for steady-state models as every calculation step is done (and visualized) in a spreadsheet. The downside of visualizing all the data is that the spreadsheet is filled with information that does not necessarily interest the end user. The problem is overcome in HSC by hiding all unimportant data columns.

Most mineral processing units are currently implemented as DLLs. Unlike Excel macros, Sim DLLs follow the "separation of concern" principle, where models and views are separated from each other. All the calculations are done in the model, which returns the data to the view. The view then renders the data in an Excel spreadsheet. DLL models do not rely on auto-generated cell formulas and calculation should in theory be 2-4 times faster than the corresponding Excel model [24].

2.5.2. Controls

Sometimes it is necessary to adjust variables according to one or more parameters. One example would be adjusting the airflow to a desired air-fuel ratio. HSC Sim's unit operations can be adjusted with a set of different controllers. Steady-state simulations have 4 different

iterative controllers that solve the steady state from either the relative value difference or their derivate. Dynamic simulation uses PID controllers, which are significantly faster than iterative controllers. HSC Sim also contains custom sheets to provide more detailed custom calculations for the end user. The custom sheets can be used for implementing control variables and conditions.

2.5.3. Steady-state process simulation

Steady-state simulation in HSC is conducted through solving the mass and heat balances. The mass balance is used to determine whether or not a reaction is possible.

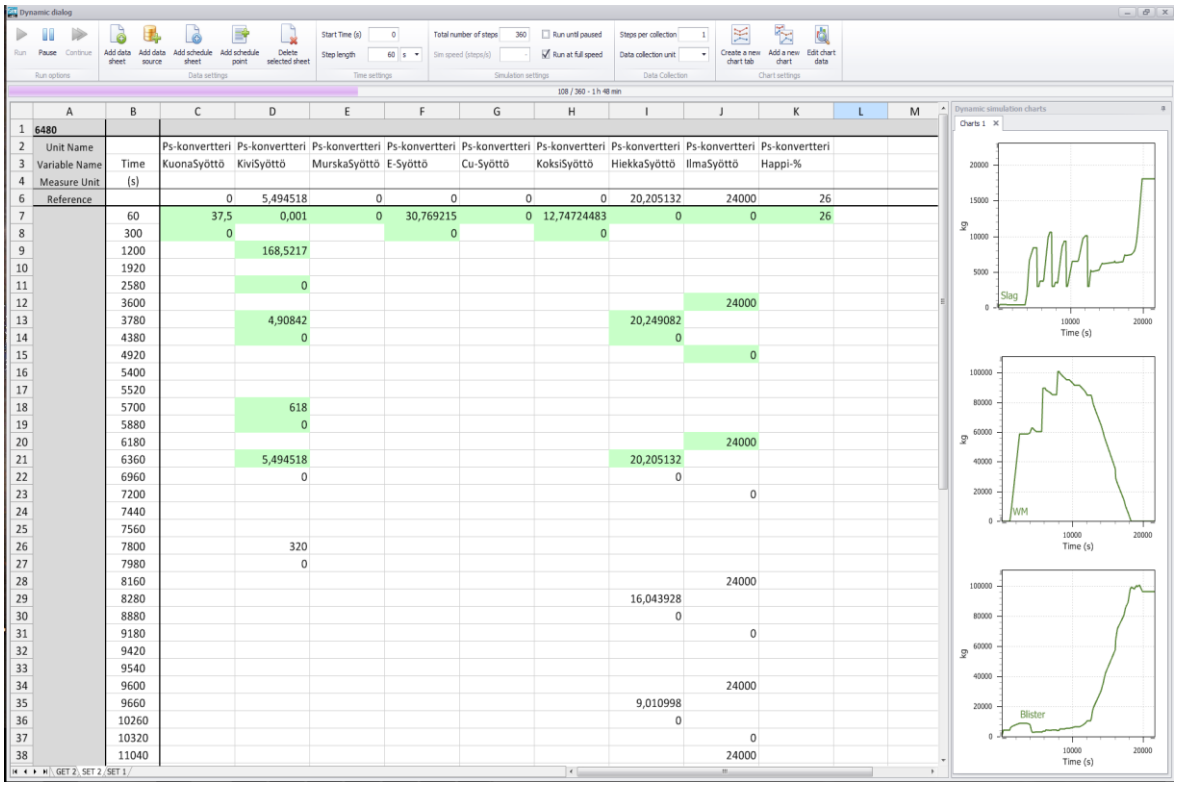
The heat balance in steady-state models is calculated from the enthalpy difference between the input and output streams, which means that the user is required to specify an output temperature for each operation unit. The equilibrium temperature can be solved by using controllers that iterate the output temperature relative to the heat balance. The advantage of using controllers is that the user is free to specify the behaviour. The disadvantage is that controllers are slower to calculate. However, the calculation speed is generally not an issue in steady-state calculation.

Beside Excel sheets, many steady-state units contain various wizards. These wizards can for example model chemical reactions or chemical equilibria. Wizards were mainly used in older HSC models, and have in recent years been replaced with DLL units.

2.5.4. Dynamic process simulation

At the time of writing, dynamic simulation has not yet been released for HSC Sim and some of the features are still open for discussion. Therefore, the principles of dynamic simulation will only be explained briefly.

Dynamic simulation in HSC is a discrete process with a fixed time step. The simulation follows a predefined time schedule that performs a set of actions at a given point in time. Data collection is performed after each simulation step for a set of user-specified parameters. Simulation data can be accessed as both raw data and visual charts, as seen in the right tab in Figure 5.



	A	B	C	D	E	F	G	H	I	J	K	L	M
1	6480												
2	Unit Name		Ps-konvertteri	Ps-konvertteri	Ps-konvertteri	Ps-konvertteri	Ps-konvertteri	Ps-konvertteri	Ps-konvertteri	Ps-konvertteri	Ps-konvertteri		
3	Variable Name	Time	KuonaSyöttö	KiviSyöttö	MurskaSyöttö	E-Syöttö	Cu-Syöttö	KoksiSyöttö	HiekkaSyöttö	IlmaSyöttö	Happi-%		
4	Measure Unit	(s)											
6	Reference		0	5,494518	0	0	0	0	20,205132	24000	26		
7		60	37,5	0,001	0	30,769215	0	12,74724483	0	0	26		
8		300	0			0		0					
9		1200		168,5217									
10		1920											
11		2580		0									
12		3600								24000			
13		3780		4,90842					20,249082				
14		4380		0					0				
15		4920								0			
16		5400											
17		5520											
18		5700		618									
19		5880		0									
20		6180								24000			
21		6360		5,494518					20,205132				
22		6960		0					0				
23		7200								0			
24		7440											
25		7560											
26		7800		320									
27		7980		0									
28		8160								24000			
29		8280							16,043928				
30		8880							0				
31		9180								0			
32		9420											
33		9540											
34		9600								24000			
35		9660							9,010998				
36		10260							0				
37		10320								0			
38		11040								24000			

Figure 5. The schedule sheet in HSC's dynamic dialogue. The dynamic dialogue controls the dynamic calculations in HSC Sim. The figure shows a pre-release version of the dialogue

HSC Sim can run both schedule- and event-driven simulation. Event-driven simulation means that a set of actions is preformed based on one or more conditions. Event-driven simulation can also be used to investigate future behaviour based on a given scenario.

One aim of this thesis was to create a dynamic process unit which used both schedule- and event-driven simulation. The general calculation unit will be discussed in chapter 3 and the more detailed model will be discussed in chapter 4.

2.6. Peirce-Smith converter modelling in HSC Sim

PS converting is a relatively old technology, and numerous models have been implemented over the years. There are many ways to implement PS converters, and at least two different approaches have been used in HSC.

The first approach was conducted using HSC's steady-state calculation blocks. The reactions in the calculation block are based on experimental kappa distributions combined with steady-state controllers. A flow sheet model based on the Boliden Harjavalta (BOHA) smelter is illustrated in Figure 6.

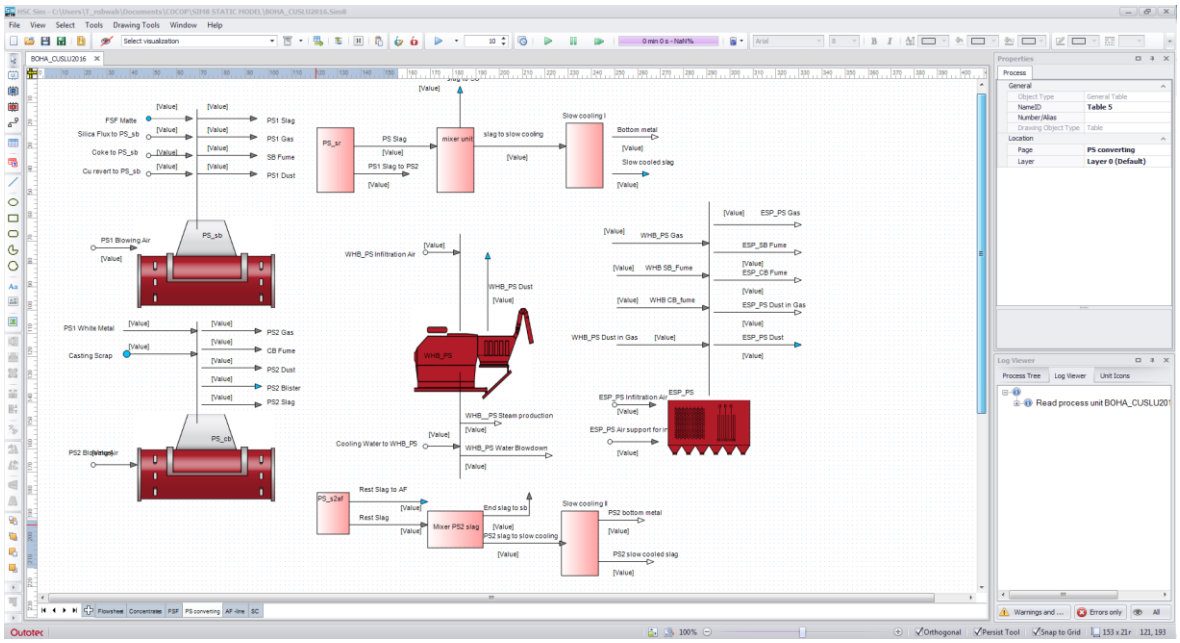


Figure 6. The converters in the steady-state Boliden Harjavalta smelter model for HSC Sim 9.

A different approach was used by Matti Hietala in his thesis [12], which included creating a model using HSC's chemical equilibrium module combined with a spreadsheet model. The model calculations are based on minimizing the Gibbs free energy in tanks. The reactions in this thesis were implemented using a similar approach.

3. HSC Sim Dynamic Pyro Unit

HSC Sim is a flow sheet based simulation software where calculation units perform operations on given compounds. HSC Sim contains a comprehensive pyrometallurgical steady-state Excel unit based on phase, species and element distributions. Although the pyrometallurgical (pyro) calculation unit contains many useful tools, it is not designed for dynamic simulation.

One of the goals of this thesis was to define, design and implement a general dynamic HSC unit for various pyrometallurgical applications. Many of the implemented tools already existed in the steady-state Excel unit, but had to be translated into DLL code. The new model also introduced new features, which were essential for modelling the process dynamics.

3.1. General principles

The three main components in the new model are streams, tanks and operations. Each of the components fulfils a smaller purpose. The purpose of the input and output streams is to move heat and content externally. Operations are used to transfer heat and content internally inside the unit. The heat and the content are conserved in tanks. Tanks can therefore only be modified through external inputs, outputs and operations. The main concepts are shown in Figure 7.

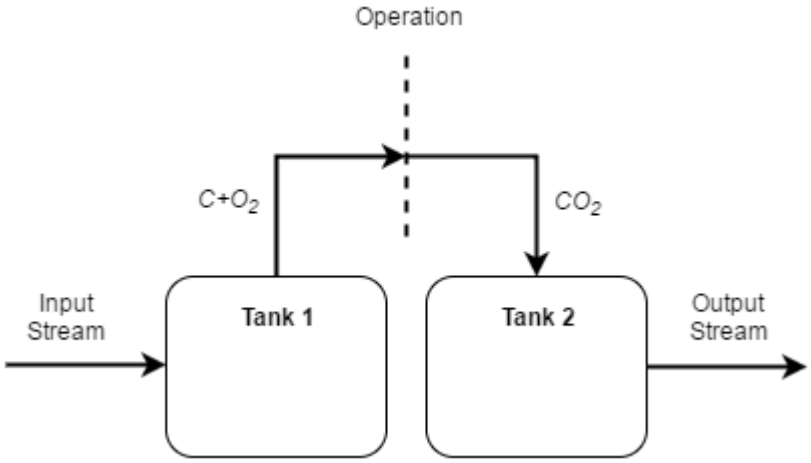


Figure 7. The diagram shows the connection between the different components in the new calculation unit. The main components include input streams, output streams, tanks and operations.

3.1.1. Inputs and outputs

Units in HSC Sim are connected through streams. Streams can be used to transfer heat and content between different calculation units. Streams in the new pyrometallurgical unit are connected to specific tanks and phases using certain distributions. Input streams are instantly mixed with the existing content. Outputs can either be removed at a constant rate or through overflow.

3.1.2. Tanks

The implemented pyro unit follows the tank principles in which energy and mass are conserved inside a system. One unit may contain many tanks with different properties. A tank consists of one or many phases that contain chemical species.

Unlike previous HSC models, the state (e.g. solid or liquid) and the species are treated separately. The state is defined through the boiling and melting point of each phase. All compounds inside a phase share a common state, which is determined from the temperature.

The enthalpy is conserved in tanks and determines the tank temperature and states. A tank may also contain heat losses or energy feeds, which impact the tank temperature as the simulation progresses. The pressure is not linked to temperature, and is thus primarily used to determine the volume of ideal gases.

Species are removed externally as output streams or as overflow. The output stream can either be moved at a constant rate or as a proportion of the current content. The overflow depends on the tank level, which is determined from the tank size. The content is always removed at the active composition and temperature.

The content or specific states of the content can also be moved internally through a reaction rate connected to a specific operation. The reaction rate moves content through a boundary area, which performs an operation on the content. The boundary area and operations will be discussed in the next section. The implemented tank user interface is illustrated in Figure 8.

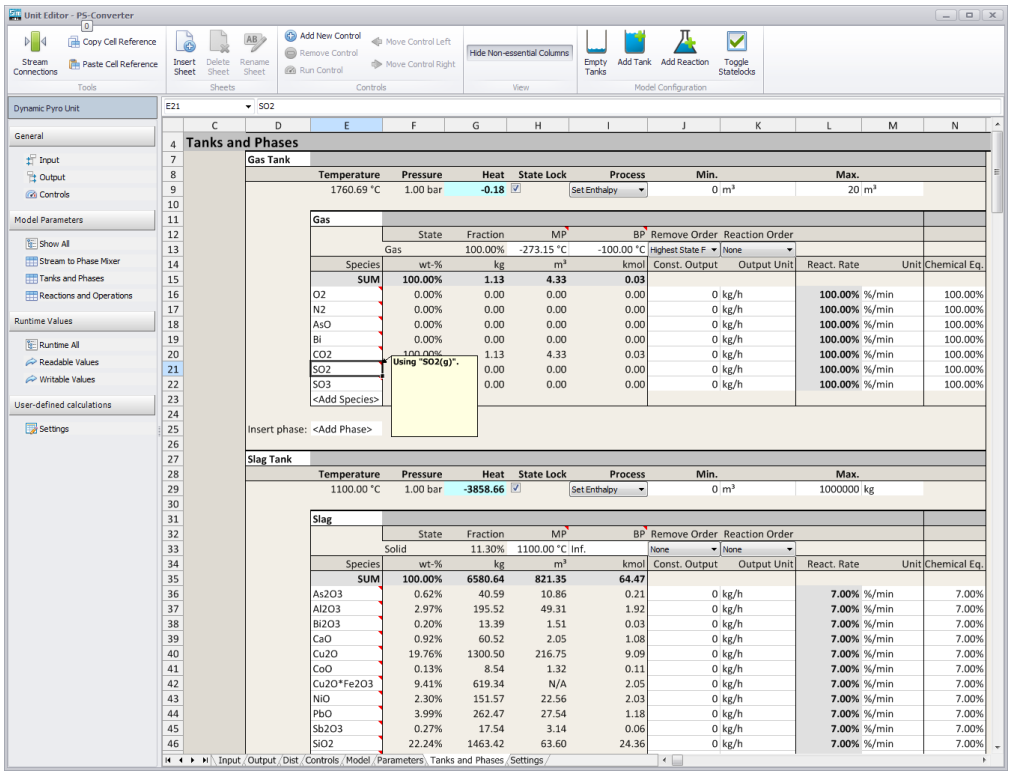


Figure 8. The user interface for the base model implemented for HSC Sim 9. The figure shows the tanks in a pre-release version of the new calculation unit.

3.1.3. Operations

Unit operations can be regarded as the boundary between two or several tanks. The main purpose of unit operations is to transfer mass and energy between tanks and phases. There are four types of operations available, as seen from the dropdown menu in Figure 9. The available operations are element distribution, chemical equilibrium, ideal mixer and ideal heat mixer.

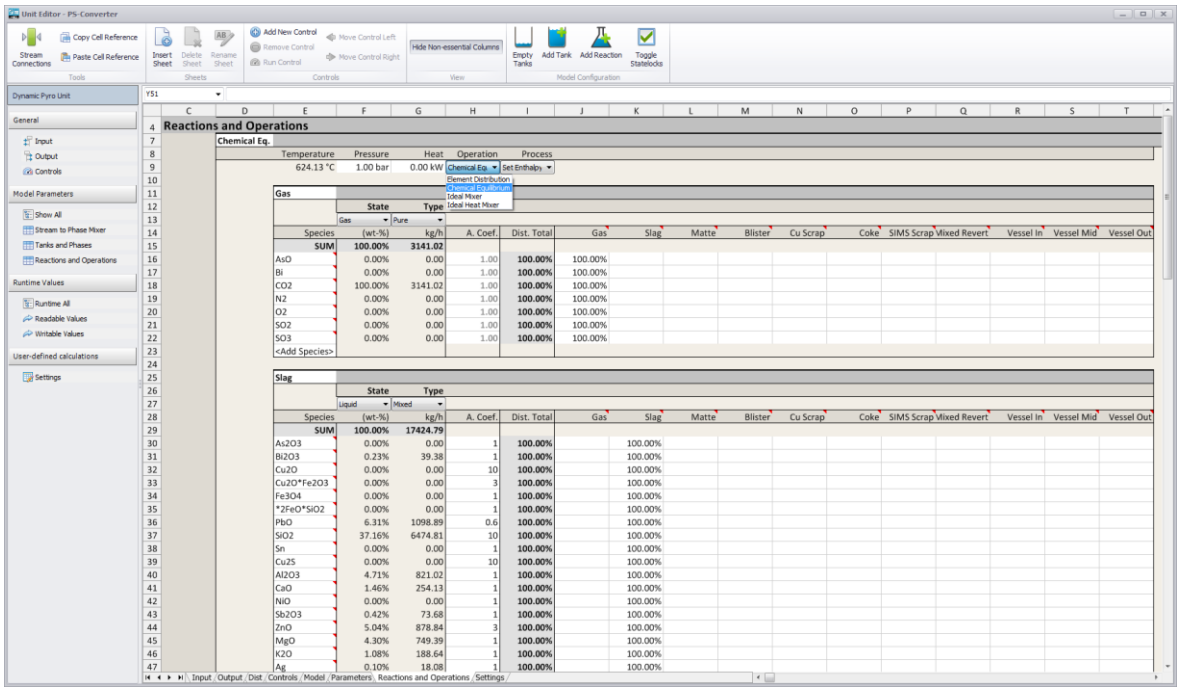


Figure 9. The user interface for the base model implemented for HSC Sim 9. The figure shows the operations in a pre-release version of the new calculation unit.

The unit operation boundary area is defined as an area where two or more immiscible phases come into contact. The boundary describes the mixing between the phases, and the flow through the boundary area must therefore be distributed back to the phases. The destination of the output is user-defined in all cases except for ideal heat mixers, for which the content is always returned to the source.

The structure of unit operations is very similar to that of tanks. Both tanks and unit operations consist of phases and species. Each phase has an active state, which unlike tanks, is fixed regardless of the temperature. The state could theoretically be implemented by using melting and boiling points instead.

The element distribution is similar to the one used in steady-state HSC models. This operation breaks all the incoming species into elements and distributes them to new phases and species as defined by the user. The input elements are distributed to phases as either "fixed", "float" or "rest". "Fixed" means that a constant fraction is distributed to the phase. "Float" is used to distribute elements according to the theoretical requirement based on other distributions. "Rest" means that only the remaining amount is distributed so that the

distribution sum is 100 %. Element distribution to species is calculated from the phase distribution and a distribution element.

Chemical equilibrium is calculated with help of HSC's Gibbs minimization solver module. As the elemental distribution operation, the operation breaks all incoming species into elements that are distributed to the user-defined phases and species by minimizing the Gibbs free energy for the system. Chemical equilibrium phases can either be pure or mixed. The chemical equilibrium of mixed phases is determined with the help of the activity coefficient.

3.2. Program architecture

The entire pyrometallurgical DLL unit consists of over 10 000 lines of code, which is divided into smaller blocks. The blocks were implemented in the vb.NET programming language for the .NET framework. The pyrometallurgical calculation units consist of four main blocks:

- **Unit:** *Handles the interactions between HSC, the calculation and the view.*
- **Calculation:** *Handles the calculation sequence and inserts/removes data requests.*
- **Data:** *Contains the tank, reaction, phase and species data.*
- **View:** *Converts the data into user-readable form.*

HSC communicates with DLL blocks through sequence calls. The sequence call in the implemented unit is handled in the unit block, which delegates the read, write and calculation actions between the calculation block and the view block. The calculation block performs the different operations, whereas the view block converts the results into user-readable form.

The view is used for reading user inputs as well as providing the user with updated values. The view was separated from the rest of the unit so that calculations could work regardless of the user interface. The communication between different blocks is illustrated in Figure 10.

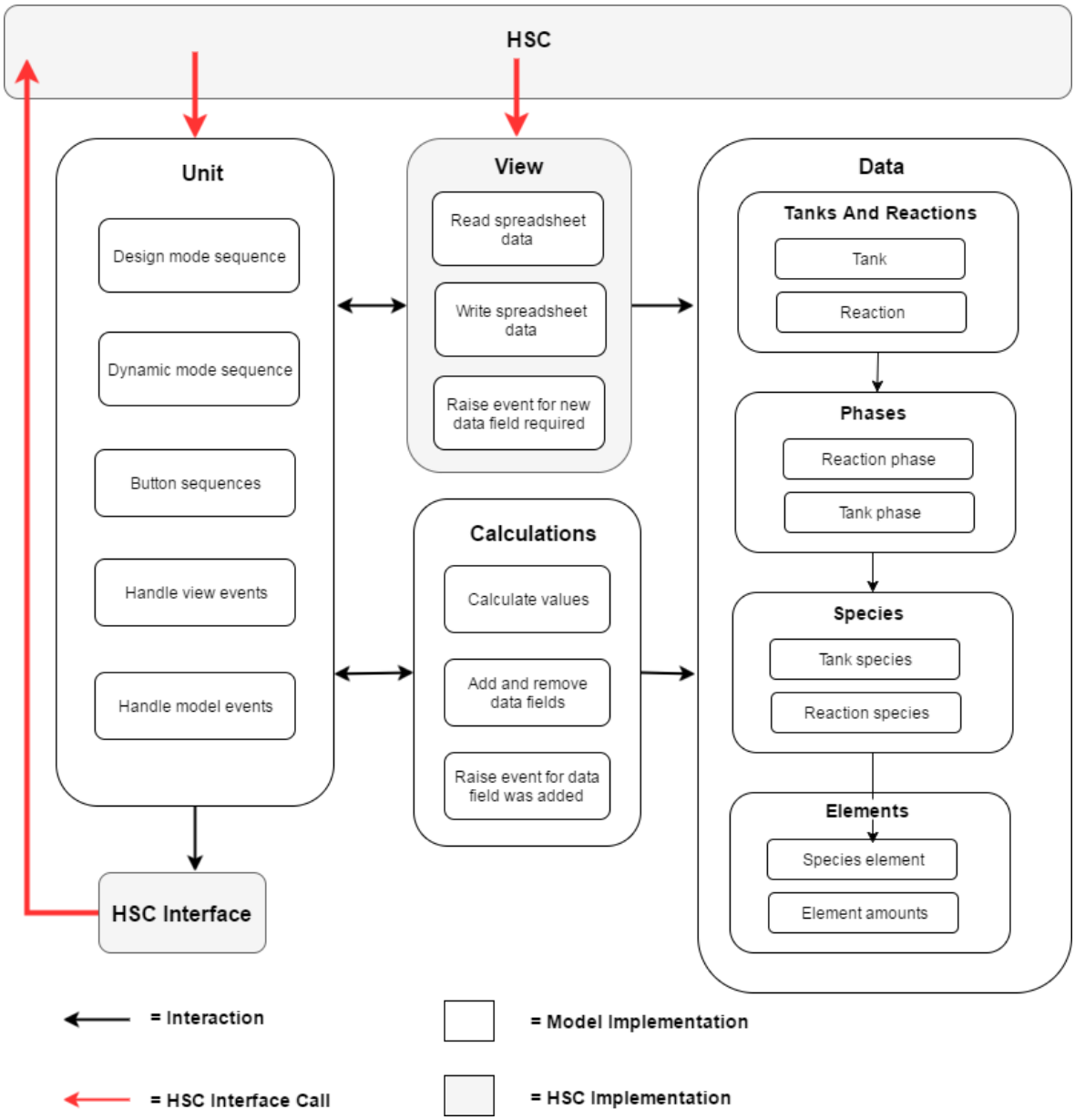


Figure 10. Program architecture for the implemented calculation unit. The blocks were implemented as separate classes.

3.2.1. Unit block

The unit block handles the communication between HSC, calculations and the view. HSC can run sequences from the unit block, which delegates commands between the calculations and the view. The DLLs in HSC must in general contain at least three sequences: one for design mode, one for steady-state calculation and one for dynamic calculation. The DLLs in HSC may in addition contain multiple optional sequences. It is also possible for users to define their own sequences, which appear as buttons on the user interface.

The design mode sequence is intended to handle user inputs whenever the calculation is inactive. Each user input will trigger the design mode sequence regardless of the action. The design mode sequence is mostly used for calculating current rates as well as converting spreadsheet data into calculation data. Data conversion is discussed in section 3.2.3.

The implemented unit was designed to be strictly dynamic, and therefore a steady-state calculation mode was not implemented. The dynamic calculation includes reading model inputs, applying operations and writing outputs.

The view and the calculation block can communicate with each other. The transmitting end sends out a request which is handled by the unit block. The unit block decides how the request is handled, thus making the view and the calculations independent from each other.

3.2.2. Calculation block

The operations are implemented inside the calculation block. The calculation block is designed to solve the state as well as control the active data and the connection between different data fields. This means that tanks, reactions, phases and species are all created and deleted inside the calculation block.

3.2.3. Data block

The data is in fact a collection of multiple smaller blocks with a similar structure. Data blocks describe the current state of streams, tanks and reactions.

The data consists of tanks, reactions, phases, species and element objects. Tanks and reactions share a similar structure, although many of the calculations are implemented individually. This means that there are typically two definitions of phases and species as well.

Both tanks and reactions use the hierarchy illustrated in Figure 11. The calculation block is on the top of the hierarchy with both tanks and reactions as children. The following objects in the hierarchy are phases, which are followed by species and elements. Each object in the hierarchy has access to its parent and its children. The parent access in newer models is slightly more restricted in order to make sure that the data hierarchy is followed.

Most of the data is stored with the hierarchy. The data for each hierarchy level is shown in Figure 11. The parameters defined on the hierarchy level are shared between both tank and reaction components. Tanks and reactions may also include operation-specific parameters.

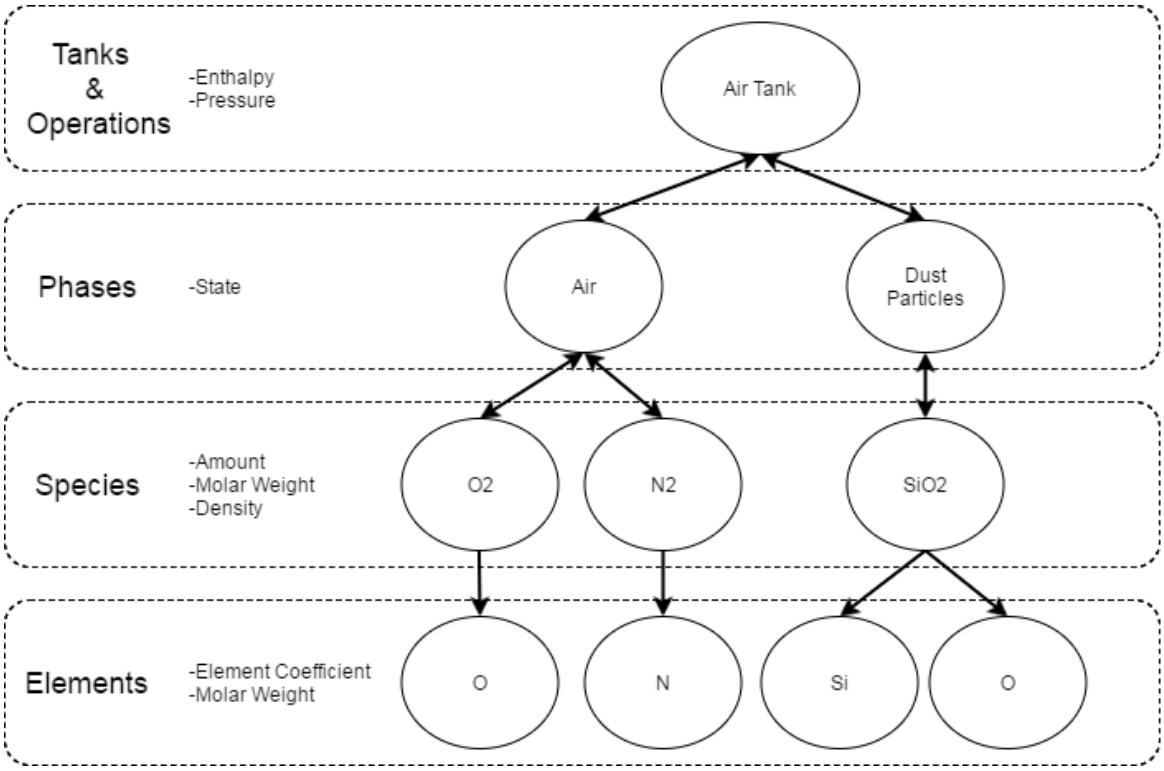


Figure 11. Hierarchy and data data fields for tanks & operations, phases, species and elements. An air tank is used as an example to illustrate the difference between tanks and phases in the new unit.

3.2.4. View block

Some background information about HSC Sim's DLL interface is required in order to understand the view block. HSC Sim is implemented using the MVC architecture pattern. The view in HSC Sim consists of Excel spreadsheets, where every action in the view is handled by a controller. The DLL contains a (simplified) copy of the spreadsheet, which is occasionally synchronized with the actual spreadsheet. The controller in the view forces the copied values in the DLL to synchronize with the Excel values. A user input would for instance refresh the corresponding data field in the DLL.

The spreadsheet data in HSC is transferred to the model through a generic data type. The advantage in having a generic data type is that any model can be programmed using one implementation on the software side. The disadvantage is that the spreadsheet data is typically too complex for models to understand. Models usually require distinct data in the form of text and numbers instead of large collections of data.

A data type converter was developed for the pyrometallurgical calculation unit in order to overcome the indistinct data problem. The data converter transformed the spreadsheet data into tank, phase and species data. A similar converter was implemented in the opposite direction in order to transform the model data back into spreadsheet data. In this thesis the data type converters are (inaccurately) referred to as a view, although the view block only works as a (data converter) controller for the existing view component.

DLLs in applications such as HSC Sim are traditionally designed to be pure calculation components. The idea is that programmers do not need to know about the view, thus allowing

them to focus on the calculation. The view block was therefore implemented as a middle component, so that the actual calculations would not rely on the view. The communication between HSC and the view block is illustrated in Figure 12.

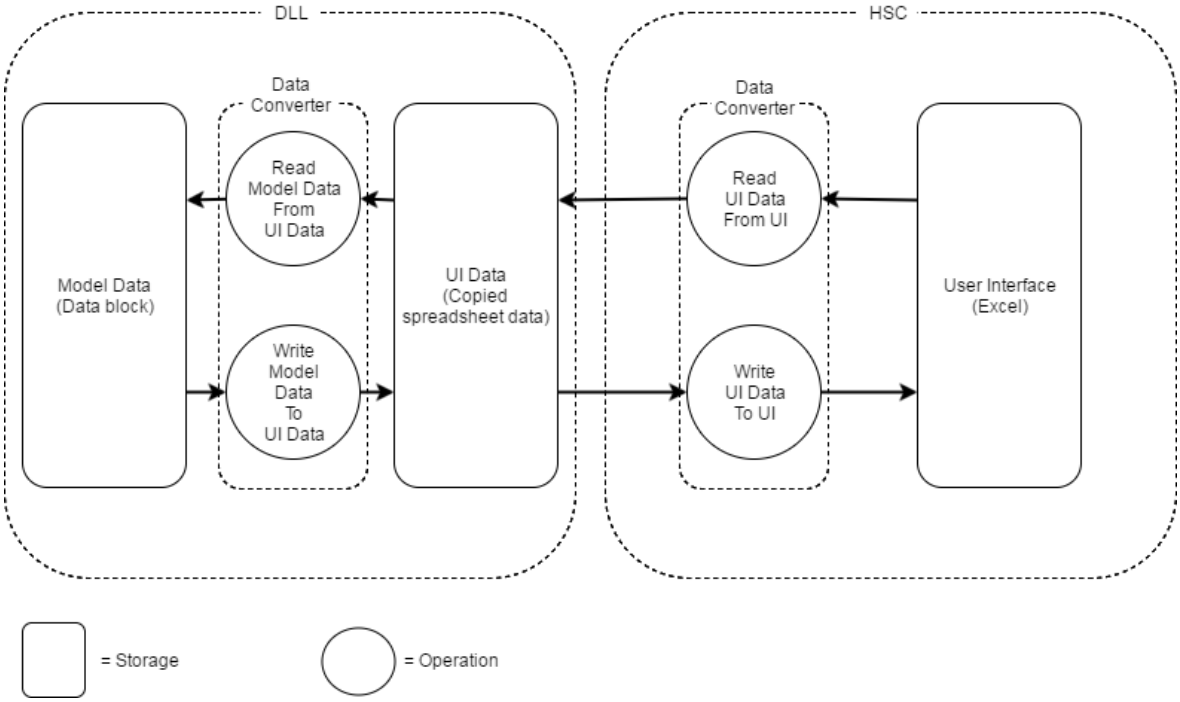


Figure 12. The communication between the Excel user interface, HSC, and the new calculation unit.

3.3. Algorithms

The scope was to implement the new unit using as much of the existing code as possible. Element distributions, chemical equilibrium and ideal mixers all existed in steady-state Excel units beforehand, and are therefore not discussed in this section.

The preliminary model was implemented with fixed states, where the content was either solid, liquid or gas, regardless of the temperature. Fixed states are typically fast to solve but less flexible in terms of dynamic modelling. Boiling and melting points were therefore introduced in order to make it easier to model different processes.

The introduction of boiling and melting points set new requirements for efficiently solving temperature and enthalpy. HSC contained multiple enthalpy and temperature solvers primarily designed for steady-state equations. The steady-state equation solvers had trouble meeting the new requirements, and were thus replaced with more efficient numeric solvers designed for repeatedly solving similar equations. The algorithms behind the new temperature and enthalpy solvers are introduced in the following sections.

Not only was it important to solve the temperature and the enthalpy, but also the state. The state was solved by comparing the boiling and melting points with the corresponding temperature. In the worst-case scenario, each possible state had to be calculated once. An initial guess was used in order to minimize the risk of the worst-case scenario. The optimized enthalpy to state algorithm is introduced in section 3.3.3.

3.3.1. Enthalpy

Enthalpy is used as the primary measurement unit of heat. It is therefore important for instance to convert boiling and melting points into enthalpy. The enthalpy can be determined by combining the heat coefficient (17) with the enthalpy function (18), see chapter 2.3.3. The resulting function (32) is used when converting both temperature to enthalpy and enthalpy to temperature.

$$h = \int_{T_0}^{T_1} (A + B * 10^{-3} * T + C * 10^5 * T^{-2} + D * 10^{-6} * T^2 + E * 10^8 * T^{-3} + F * 10^{-9} * T^3)\, dT + \Delta H \tag{32}$$

Calculating enthalpy from temperature gives equation (33).

$$h = A * (T_1 - T_0) + \frac{B}{2} 10^{-3} * \left({T_1}^2 - {T_0}^2\right) - C * 10^5 * \left(\frac{1}{T_1} - \frac{1}{T_0}\right) + \frac{D}{3} * 10^{-6} * \left({T_1}^3 - {T_0}^3\right) - \frac{E}{2} * 10^8 * \left(\frac{1}{{T_1}^2} - \frac{1}{{T_0}^2}\right) + \frac{F}{4} * 10^{-9} * \left({T_1}^4 - {T_0}^4\right) \tag{33}$$

3.3.2. Temperature from enthalpy

The enthalpy is typically converted into temperature for the user. The active temperature can be solved from function (32) given in section 3.3.1. In this case the unknown variable is the final temperature T_1. Solving for T_1 gives a sixth-order polynomial with coefficients c_1, c_2, c_3, c_4, c_5, c_6 and c_7 in equation (34).

$$\begin{cases} c_1 * {T_1}^6 + c_2 * {T_1}^5 + c_3 * {T_1}^4 + c_4 * {T_1}^3 + c_5 * {T_1}^2 + c_6 * T_1 + c_7 = 0 \\ c_1 = \frac{F}{4} * 10^{-9} \\ c_2 = \frac{D}{3} * 10^{-6} \\ c_3 = \frac{B}{2} * 10^{-3} \\ c_4 = A \\ c_5 = (h - \Delta H) - a * {T_0}^4 - b * {T_0}^3 - c * {T_0}^2 - d * T_0 - f{T_0}^{-1} - g{T_0}^{-2} \\ c_6 = -C * 10^5 \\ c_7 = -\frac{E}{2} * 10^8 \end{cases} \tag{34}$$

The sixth-order polynomial is solved using the Jenkins-Traub iteration algorithm. The results are analysed in order to find the best real number solution.

The numerical approach proved on average to be about 500 times faster compared to the corresponding algorithm used for HSC steady-state calculations.

3.3.3. States from enthalpy

The state is solved according to the boiling and melting points. The basic principle is simple: if the tank temperature is below the melting point then the state is solid, if the tank temperature is between the melting and boiling points then the state is liquid, and if the tank temperature is above the boiling point then the state is gas. The database entries are chosen according to the state.

However, the tank heat content is not defined as temperature but as enthalpy, whereas the melting and boiling points are given as temperature. A single tank can also contain multiple phases, each with both a melting and a boiling point. The number of melting and boiling points are therefore not restricted to any particular number.

An optimized algorithm is required to solve the state from the melting point, the boiling point and the enthalpy. The easy solution would be to loop through each melting and boiling point and choose the database entries accordingly. The loop can be optimized by starting near the solution in order to minimize the worst-case scenario.

The first step in solving the problem is to compare the tank enthalpy with the active melting or boiling point. In this case, the tank enthalpy is converted to temperature using equation (33) given in section 3.3.2. The starting point for the iteration loop is chosen from the previous round, which is typically quite close to the solution.

The second step is finding the melting and boiling points that conflict with the corresponding state. The ideal state is solved when no conflict is found, and meanwhile the state with the closest conflicting melting or boiling point is changed. The direction of the loop is chosen according to the current state. The loop is repeated until no conflicts are found or as long as the direction of the loop stays the same.

A phase may simultaneously contain two states, in which case the loop will not approach a solution. Instead, another algorithm is used to evaluate the ratio between the two states. The fraction is solved using enthalpies around the active melting or boiling points according to equation (35).

$$\lambda_{state\ fraction} = \frac{h_{max} - h_{tank}}{h_{max} - h_{min}} \tag{35}$$

The tank temperature is always equal to the melting or boiling point if multiple states are present. The database entries are chosen according to all active states.

3.3.4. Equilibrium temperature

Heat is transferred to reactions as enthalpy. The chemical equilibrium in HSC is calculated at a fixed temperature. The active reaction temperature for the implemented calculation unit is determined from the input enthalpy and the output composition. The output composition, however, is determined by the chemical equilibrium, which results in a dependency between thermal and chemical equilibriums.

The algorithm uses iteration in order to find the theoretical reaction temperature. The chemical equilibrium is calculated starting from the equilibrium temperature that was solved in the previous calculation round. The temperature is updated from the new composition, which is compared to the previously used temperature. The solution is found if the new temperature is within 1 Kelvin of the previous temperature. Otherwise, the process is repeated until the precision is achieved or until the iteration no longer approaches a solution.

A precision of 1 Kelvin has been tested and found to be quite accurate, as a small temperature difference will have a relatively small impact on the compositions. The total enthalpy in the reaction remains fixed regardless of the calculated temperature.

4. Modelling

In August 2014, a sampling campaign was performed during the SIMP project. The sampling consisted of 10 converter batches performed under different conditions. Previously, a Matlab model had been tested using the sample data. [25]

The second goal of this work was to model a PS converter using the new HSC Sim unit. The HSC Sim model was built utilizing the existing Matlab model. The emphasis was to demonstrate the efficiency of generic pyro unit in very challenging PS converter modelling. This work excludes the fine-tuning of the model.

4.1. Available data

The model inputs and outputs were based on batch data from the SIMP project. The batch was controlled by an operator, who was responsible for adding and removing content to and from the converter. The batches contained variations in input feed amounts and compositions as well as waiting times, and each batch was therefore operated in unique conditions. The primary feeds for one batch are shown in Table 2.

The composition of the inputs was estimated from the average sample. For instance, the Cu % in matte varied between 60-70 %, but a fixed Cu % was used for all matte feeds in the same batch. Sand, scrap and reverts were added to the process in order to control the temperature and circulate the material. Sample analyses of the different reverts were unfortunately not available. Instead, a rough estimate based on previous processes was used for the compositions. Raw element samples were processed by metallurgy specialists before they could be added to the model.

The copper concentrate in blister is slightly lower than that found in the literature (partly due to the relatively high amount of impurity components), while the copper concentrate in slag is slightly higher than that in the literature. The sampled slag analyses are unlikely to be pure, and probably contain small fractions of matte. The same goes for blister, which is likely to contain small fractions of slag.

Some inputs, like molten matte, were modelled to dissolve immediately into the corresponding phases. Other inputs, such as scrap metals, were modelled to dissolve only above certain temperatures or after melting.

Table 2. Available input and output data for an example batch.

Time	*Matte (In)*	*Silica (In)*	*Coke (In)*	*Scrap & Reverts (In)*	*Slag (Out)*	*Blister (Out)*
00:00-10:00			*2.0*	*11.2*		
10:00-11:00	*32.8*					
11:00-12:00	*32.3*					
12:00-13:00	*31.6*	*4.6*		*6.5*		
13:00-14:00	*15.5*	*2.8*			*11.4*	
14:00-15:00	*30.5*				*9.8*	
15:00-16:00		*1.4*			*9.5*	
16:00-17:00	*26.6*	*2.5*			*13.2*	
17:00-18:00				*8.6*	*16.5*	
18:00-19:00						
19:00-19:40					*3.9*	*128.1*

4.2. Tanks and phases

The converter was divided into layers in order to simulate the individual slag, matte, blister and scrap temperatures. Layers represented tanks, which in turn consisted of one or more phases. Most of the layers used consisted of a single phase, but components with similar properties were modelled into shared layers. Most of the heat calculations were done using the layer properties.

Each layer consisted of species and elements. An element analysis of each layer was available from the SIMP project, but the specific compounds had to be determined by other

means. Matti Hietala's thesis [12] was initially used to determine the species in each layer, but the data was later modified based on feedback from modelling experts [26]. It was essential to use the right compounds in order for the "Gibbs minimization" algorithm to correctly solve the chemical equilibrium. Table 3 shows the estimated species in each layer. A few important components, such as different silicates, were unfortunately missing from the estimates.

Table 3. ***The primary species in gas, slag, blister and matte. Less significant components are not shown in the table.***

Slag	*Blister*	*Matte*	*Gas*
Al_2O_3	Ag	As_2S_3	CO_2
As_2O_3	Bi_2O_3	Cu	N_2
Bi_2O_3	Bi_2S_3	Cu_2S	O_2
CoO	Cu	FeS	SO_2
Cu	Cu_2O	Ni_3S_2	SO_3
Cu_2O	Cu_2S	PbS	
$Cu_2O*Fe_2O_3$	Cu_2Se	ZnS	
Fe_2O_3	Cu_2Te		
Fe_3O_4	Cu_3As		
FeO	Ni		
$2FeO*SiO_2$	Pb		
K_2O	Sb		
MnO			
$NiFe_2O_4$			
NiO			
PbO			
SiO_2			
$ZnFe_2O_4$			
ZnO			

The process was simplified by excluding dust particles from the model. The behaviour of dust was difficult to describe with the current version of the calculation unit. Instead, fractions of the impurities that are typically removed with dust were added to slag and blister.

The interaction between two layers was described through reaction rates. The interaction between the layers was estimated to be a function of the layer content, although more accurate results could be obtained by solving the interacting area between the layers. As an alternative, appropriate formulas for the reaction rates were found experimentally. For instance, it was estimated that the matte would interact with the surrounding layers at a much higher rate than blister and slag during the slag blow.

Spills and splatters were for the most part neglected in the model, although a small fraction of the measured matte feed is typically lost in a real-world application. The use of oxygen was modified to compensate for the increase in matte. A well-functioning converter retains 90-95 % of the oxygen, whereas all of the available oxygen was retained by the model.

4.3. Operations

Layers were connected through reactions, which represent the boundary area between different phases. The boundary layer was constantly in chemical equilibrium determined by certain activity coefficients. The thermal equilibrium was determined for the reaction based on the temperature of the surrounding layers, which means that the reaction also conducted heat between the layers. Reactions could additionally be endothermic or exothermic, thus absorbing or releasing heat to the surrounding layers.

The boundary area was modelled through chemical equilibrium for various reasons. The chemical equilibrium was easier to implement compared to the formula-based element kappa distributions normally used in HSC Sim pyro models, which require large amounts of data. In addition, the behaviour of the chemical equilibrium could be modified using experimental activity coefficients.

Activity coefficients were collected from the literature and old HSC models [12]. Unfortunately, some of the activity coefficients were unavailable, and were therefore determined experimentally.

4.4. Heat transfer

A detailed heat balance was modelled using custom Excel formulas. The heat balance consisted of heat radiation, conduction through the vessel, and internal heat transfer between the layers. Heat was also removed with the off-gas.

The radiation heat loss was modelled according to the radiation heat formula (22) given in section 2.3.4, which describes the heat transfer between hot and cold areas. The cold area was approximately 600 °C, and the hot side was approximately the temperature of the slag. The radiation heat loss focused on the slag, which is typically on the converter's surface. The heat reflection from dust particles was to some extent included in the cold area temperature approximations.

The vessel was divided into a thin inner layer and two thick outer layers. The surrounding temperature was estimated to be 100 °C whereas the converter temperature was calculated as a weighted average from the content. The vessel consisted of bricks including mainly magnesium oxide (MgO) and chromium dioxide (CrO_2). The material properties were taken from the HSC database and the Matlab model.

The internal heat transfer was estimated as linear to the temperature difference between the phases. The scrap metals were estimated to have a large heat transfer coefficient in order to better model instant melting. The heat conduction between slag, blister and matte was found by trial and error.

4.5. Schedule

Two batches were simulated based on the SIMP campaign data. A separate schedule was done for each of the batches. The purpose was to roughly calibrate the model according to the data. No fine-tuning of activity coefficients was done.

The full schedule of the first batch can be found in Appendix 1. The original batch was almost 30 hours long and included a 20-hour waiting time. Matte was added a total of six times, silica a total of five times and various kinds of revert materials a total of seven times. The first reverts and coke inputs were added almost a day before starting the slag blow, at which point the simulated temperature of the inner layer of the converter was still warm from the previous batch. The simulation contained five slag skims.

The second batch of 12 hours was very similar to the first batch in terms of schedule. However, the converter was not cooled between batches, and the starting temperatures were thus significantly higher than in the first batch. The matte composition in the second batch was slightly different compared to the first batch.

5. Results

A time step of one minute was used in the simulations. The compositions and the temperature data were collected once a minute after each calculation step. The results were compared to measured data and literature data in order to verify the simulation. A second batch was modelled using a different schedule in order to validate the approach. The results were finally compared to similar PS models modelled in HSC and Matlab.

5.1. Process

Comparing the simulated process in Figure 13 with the measurements obtained in the SIMP project suggests that the simulation model produces about 10-15 tonnes of extra blister. The behaviour can partially be explained by the remaining unoxidized sulphur in the blister, which will be analysed in section 5.3. Some of the copper and some of the impurities are typically removed as dust and spatters. The dust and spatter were not included in the model.

There is one uncertain issue concerning the conditions that determine how slag is removed from the converter. The molten slag and the solid slag crust are typically skimmed after each slag blow. Some of the slag may stick to the converter walls when the converter is cold, thus forming a separate solid phase that is not removed with the skimming. This separate phase was unfortunately not included in the preliminary model, which resulted in excessive quantities of slag being removed, especially in the first skims.

The results in Figure 13 suggest that the fifth slag skimming was unsuccessful. This is most likely the consequence of the previously discussed issue regarding the conditions in which slag is removed from the converter. The unsuccessful skimming could also be caused by the formation of slag from matte and silica, which will be discussed in section 5.3.

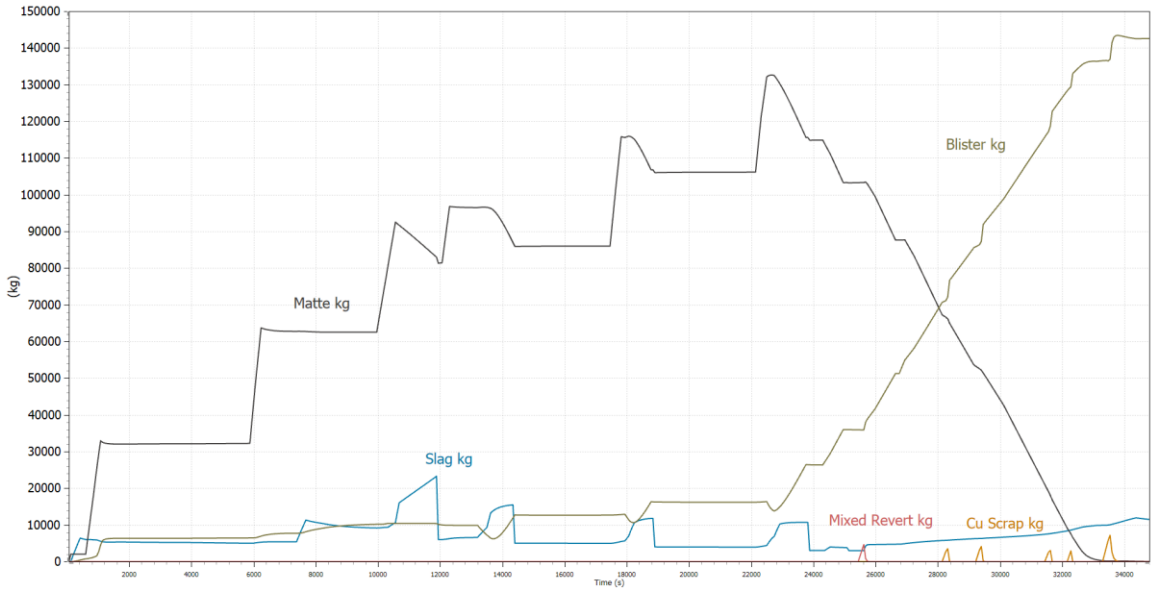


Figure 13. The converting process of matte into blister according to the simulation model.

The simulated process behaviour is considered normal despite the uncertainties with slag. The formation of blister is quite similar to that found in the measurement data.

5.2. Temperatures

The temperature profile of the simulated batch is shown in Figure 14. When the temperature is at the melting point, some of the material is solid and some is liquid. The melting process is shown by the straight horizontal temperature lines in Figure 14. The slag is influenced by heat radiation through the converter mouth and is thus slightly cooler than both the matte and blister.

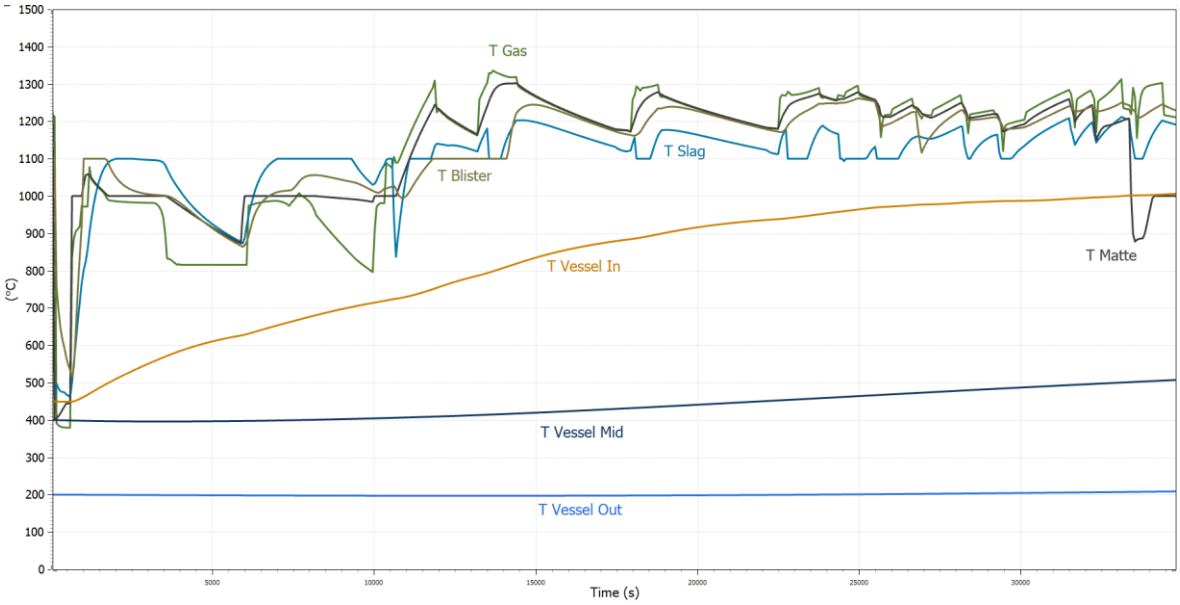


Figure 14. The simulated temperatures for the PS converter batch.

One of the issues addressed when making the model was estimating the melting point of slag, which depends on its composition. A fixed 1100 °C melting point was used for the slag despite the fact that slag may be solid at temperatures well beyond the melting points in the model. High concentrations of certain components may form a solid layer even at high temperatures, which makes the melting point difficult to describe through a fixed temperature. It is critical to model the melting point of slag correctly, as only molten states are allowed in the reaction.

The melting points for matte and blister are around 1000 °C, according to Davenport [4]. The melting points of matte and blister are well below the operating temperatures, and will thus have a significantly smaller impact on the end result compared to the melting point of slag. A relatively low melting point of 800 °C was used for scrap metals in order to simulate immediate melting.

Comparing the temperatures in Figure 14 with the corresponding literature data suggests that the simulated temperature is quite close to the actual operating temperature. The typical operating temperature according to Davenport [4, p. 133 & 138] is between 1200 °C and 1250 °C, and the temperature is especially high during the formation of slag.

5.3. Compositions

The copper, iron, sulphur and silica compositions were collected once a minute for matte, slag and blister. Full analyses were taken at given intervals to compare simulated data with measured data.

The simulated copper content for slag is 5-20 %, for matte 60-75 % and for blister 87-98 %. The copper content for matte and blister in Figure 15 is quite similar to the samples from the SIMP project. The copper in slag is expected to rise as sulphur and iron is removed from the process. However, the simulated Cu % for slag in Figure 15 remains nearly constant even after all the iron and sulphur have been removed.

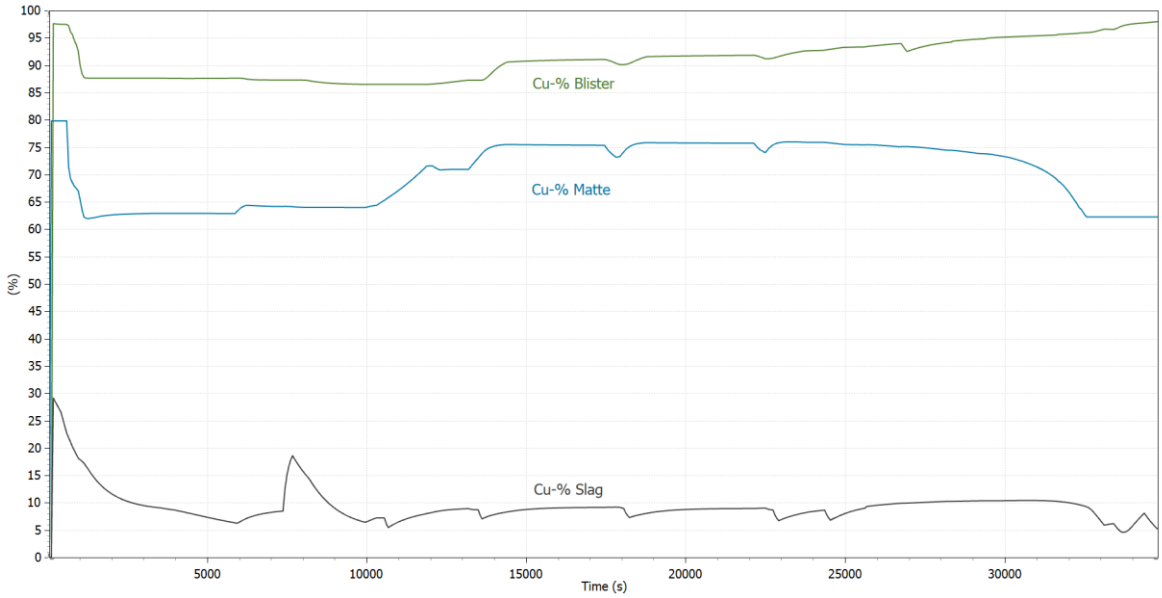


Figure 15. Cu grades of blister, matte and slag according to the simulation model.

The chemical equilibrium produced large quantities of iron oxides. Almost all the iron oxides were distributed to the slag phase, which led to a rapid drop in the Fe % of the matte, as illustrated in Figure 16. Slag was therefore only produced whenever there was iron in matte, as shown in Figure 13 in section 5.1.

The chemical equilibrium produces iron in the form of fayalite ($2FeO*SiO_2$), which means that there is at least one SiO_2 molecule for every two FeO molecules. Fayalite is produced when the silica in the slag reacts with the iron in the matte and the oxygen in the air. Using a fixed melting point for slag makes all the silica available for the chemical equilibrium whenever the temperature is above a certain point. Fayalite is thus produced at a much higher rate than normal and quickly consumes the iron from matte.

Most of the problems with the formation of slag can be solved using a more complicated formula for the melting point of slag. Sand could be added to a separate phase, from which the sand could be dissolved in slag to form fayalite.

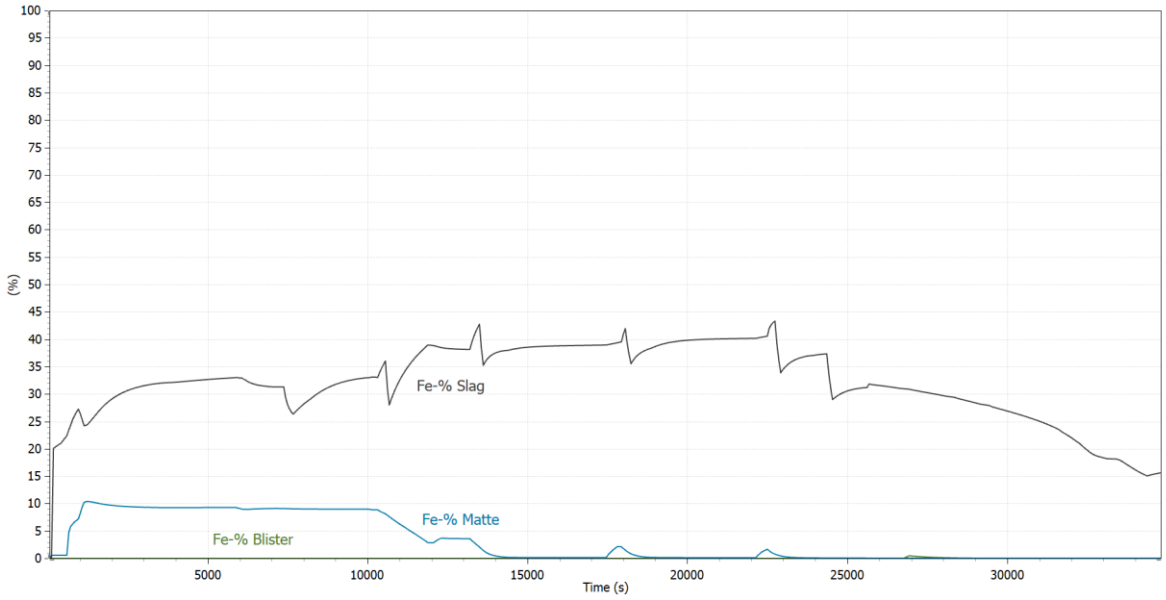


Figure 16. Fe content of blister, matte and slag. The blister contains very little iron, and is partially hidden below the x axis.

The immiscibility region can be investigated from the sulphur diagram in Figure 17. The immiscibility region for blister and matte is between 1 and 20 % according to Davenport [8, p. 135]. Comparing the blister production in Figure 13 with the sulphur content in Figure 17 suggests that most of the blister is produced in the immiscibility region.

The high sulphur content in the off-gas (see Figure 17) suggests that the batch did not quite finish. The length of the copper blow is typically determined from the SO_2 content in the off-gas, which in the simulation model is relatively high near the end. Typically the measured SO_2 content in the off-gas is about 0.3 % at the end of a batch.

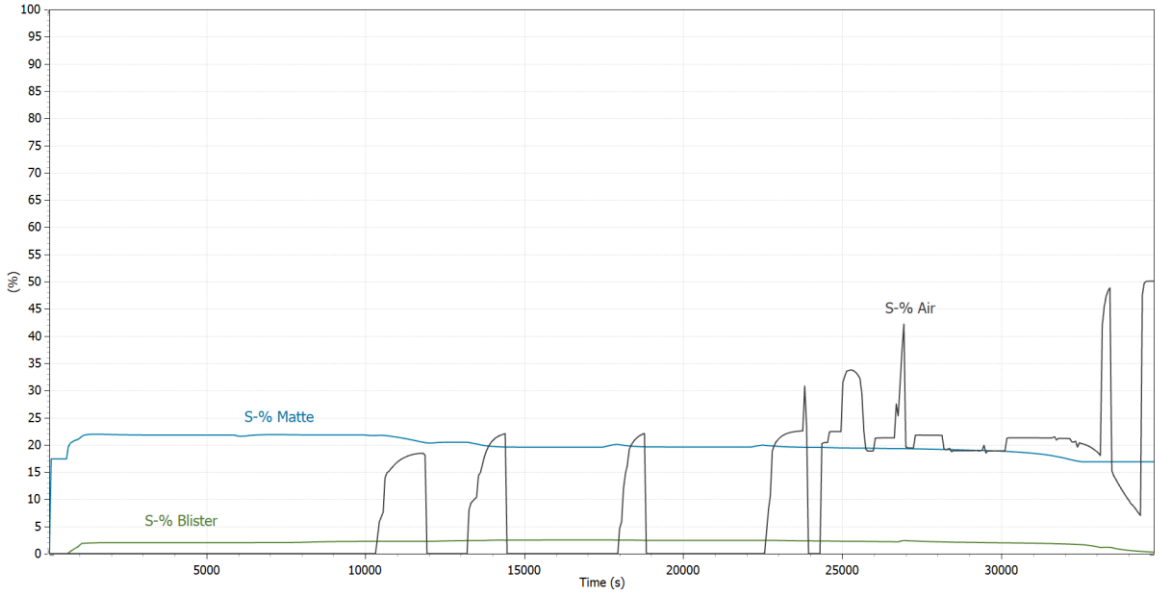


Figure 17. Sulphur weight % in blister, matte and air.

The silica content in slag is between 20 and 40 % as shown in Figure 18. The silica content in slag will affect the oxidation of iron from matte as discussed previously. The SiO_2 % will also impact the melting point of the slag.

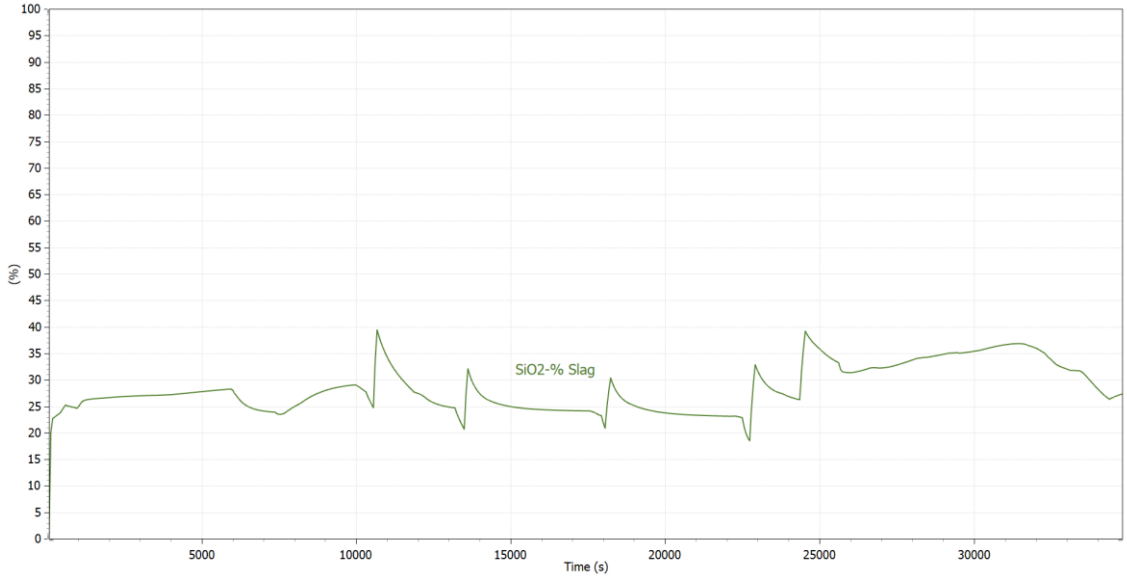


Figure 18. Silica weight-% in slag.

The composition of slag was compared to the SIMP samples, and the results are shown in Table 4. Some of the simulation data was excluded as a result of insufficient simulation data. The results suggest that slag blasting produced excess iron oxides and silica.

The differences in Table 4 can be explained by the separate solid slag phase that is formed on the converter walls but was excluded from the model, as mentioned in 5.1. Restricting the rate at which silica is dissolved into the slag could also increase the accuracy of the model.

Table 4. Absolute differences for slag in the simulation model compared to the measured data after each skimming.

Element	*Difference 1*	*Difference 2*	*Difference 3*	*Difference 4*	*Difference 5*
Fe	*+7.5 %*	*+14.6 %*	*+11.5 %*	*+11.2 %*	*N/A*
S	*+1.4 %*	*-0.8 %*	*-0.03 %*	*-0.3 %*	*N/A*
Cu	*+1.0 %*	*-7.6 %*	*-5.4 %*	*-8.5 %*	*N/A*
SiO_2	*+3.95 %*	*+2.3 %*	*+0.08 %*	*+1.3 %*	*N/A*

Table 5 shows the measured and the simulated element analysis difference for blister. The sulphur content in blister is quite high compared to the SIMP samples, which suggests that the simulated batch did not finish, as analysed earlier from the sulphur content in the off-gas. Typically blister contains very little sulphur. Instead, the SIMP samples indicate that some of the copper was over-oxidized into copper oxides.

The large quantities of sulphur in the blister (see Table 5) are a consequence of disregarded spills and spatters. The simulated blister also contained high quantities of impurities, such

as arsenic, bismuth and lead, which are typically removed with slag or as dust particles [4, p. 135].

Table 5. The absolute differences for blister in the simulation model compared to measured data.

Element	*Difference*
Cu	*+0.00 %*
Ni	*+0.23 %*
O	*-0.65 %*
S	*+0.28 %*
Zn	*+0.17 %*
Bi	*+0.14 %*
As	*+0.03 %*
Pb	*+0.31 %*

The results in Table 4 suggest that the model still requires calibration in order to properly model slag compositions. The blister compositions were, apart from the lack of oxygen, close to the measured values, as seen in Table 5.

5.4. Cooling

The converter had been empty for almost a day before starting the slag blow, and the simulation schedule was thus extended in order to take cooling into account. In the 30-hour simulation, coke and revert were added almost one day in advance and the circulated end slag was added a few hours beforehand.

The process behaviour for the full version was almost identical to that of the shorter version. The blister Cu % after the simulation was almost the same with minimal differences in other compositions, mostly caused by different temperature profiles at the beginning. The full converter batch is shown in Figure 19.

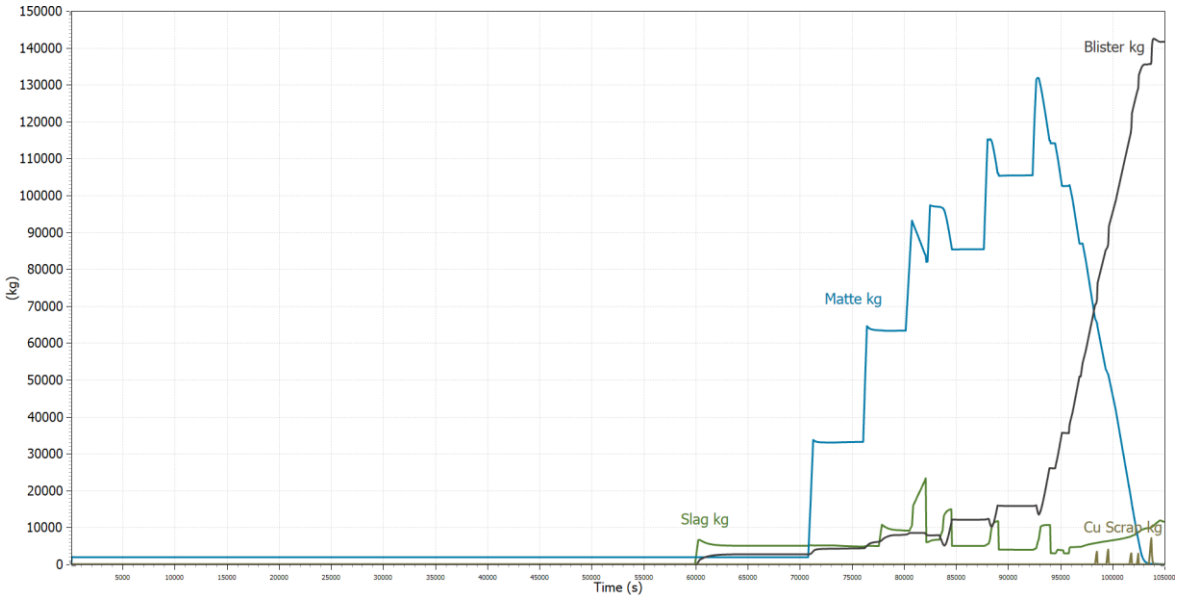


Figure 19. Full batch process according to the simulation.

The cooling temperature was dominated by the vessel's large heat capacity. The simulated converter temperature dropped by about 400 °C over the 20-hour cooling as shown in Figure 20. The process temperature behaviour for the process was quite similar to the shorter version, apart from small temperature variations at the beginning.

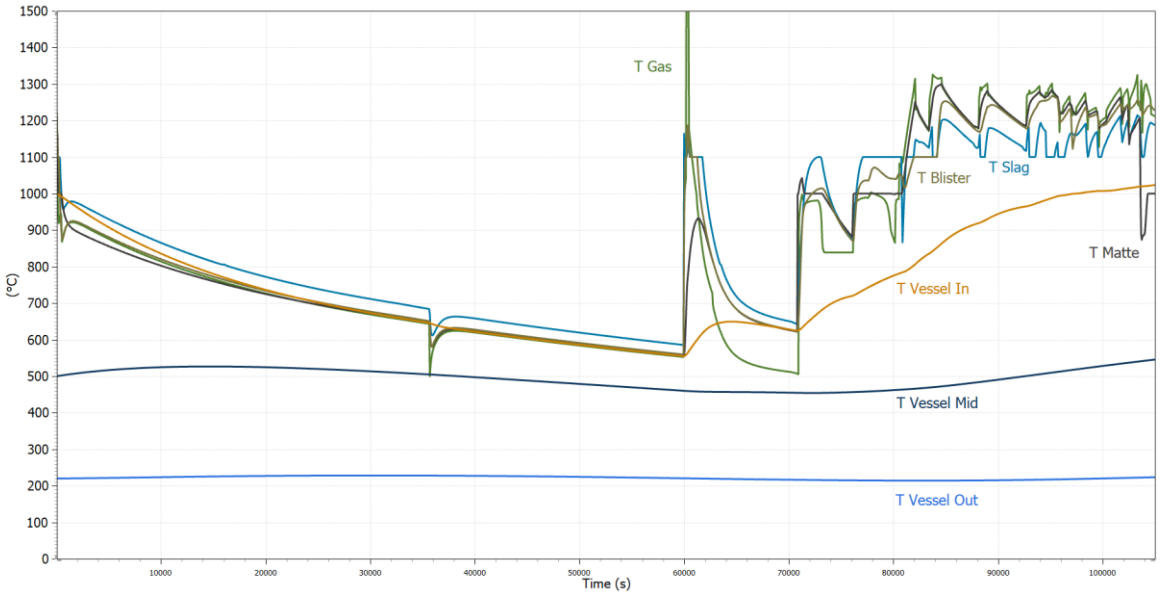


Figure 20. Temperature profile with the full schedule. The converter stood almost empty for approx. 20 hours.

5.5. Validation

A second batch was tested in order to verify the configuration. The element analyses were converted into species with the HSC "element to species" converter. The second batch was conducted using the same converter as in the first batch, but the schedule was modified based on the new data. Some of the unavailable input samples were copied from the first batch.

Figure 21 suggests that the second batch behaved like the first batch. Slag and blister were formed from matte during oxidization. The Cu % of blister for the second batch was close to that of the first batch, although this time the actual sample data was unavailable.

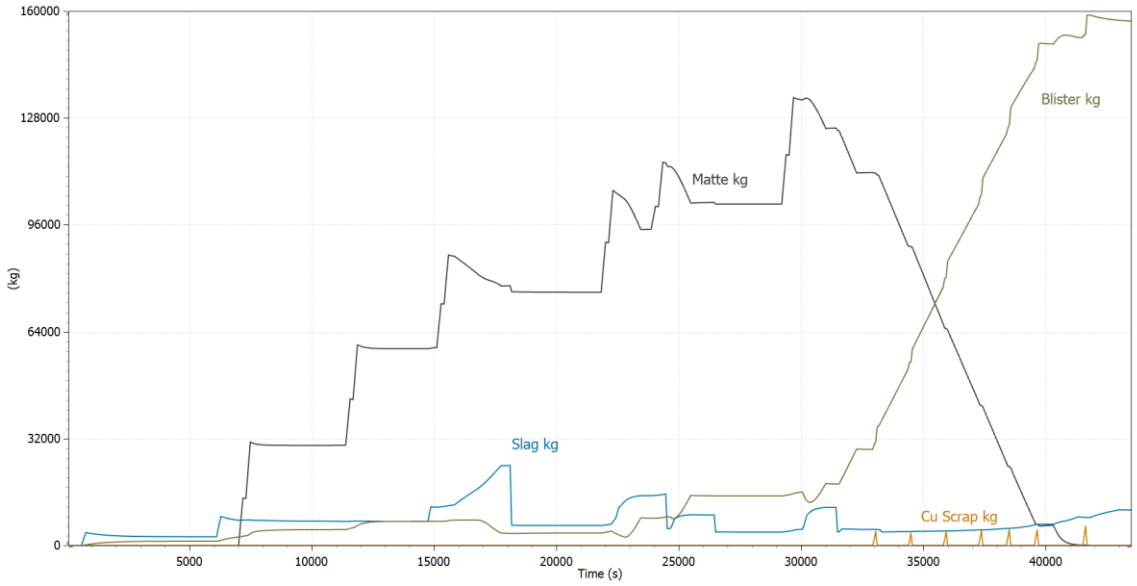


Figure 21. Quantities produced in the second batch according to the simulation model.

The temperature behaviour shown in Figure 22 is quite similar to that of the first batch. However, the starting temperatures of the vessel were quite different as the converter was still warm from the previous batch.

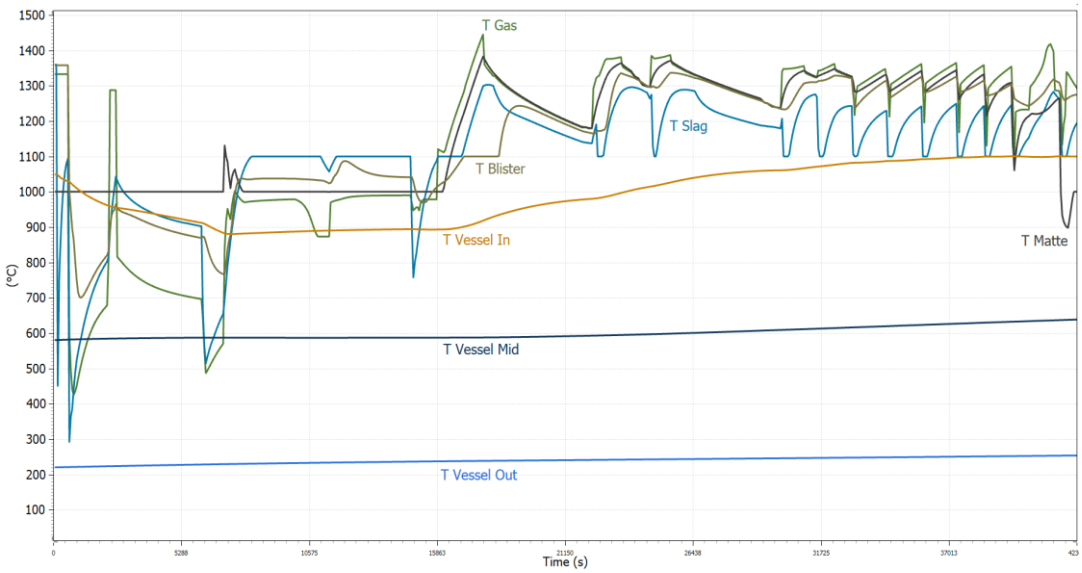


Figure 22. Temperature profile of the second batch according to the simulation model.

The overall result for the second batch was very similar to the first batch. The differences in both scheduling and starting temperatures had a relatively small impact on the end result. Both batches contain the same flaws, mainly because of issues with separate slag phases, silica, and melting points, as discussed in previous sections.

5.6. Previous HSC models

Matti Hietala [12] created a converter model in HSC 7 using a simplified approach. The heat calculations were excluded from the process, which meant that the converter was operated

at a constant 1200 °C. The converter was constantly in chemical equilibrium, meaning that reaction kinetics were not taken into account. However, the model can be used as an indication of the expected result from PS converter modelling using chemical equilibrium.

The results of Matti Hietala's thesis shown in Figure 23 suggest that chemical equilibrium forms slag at the expense of both blister and matte. The blister was well over-oxidized as a result of instant chemical equilibrium. These problems were (over) compensated in the new model using more complicated reaction kinetics. The real process behaviour should be somewhere in between the previous converter model and the new converter model.

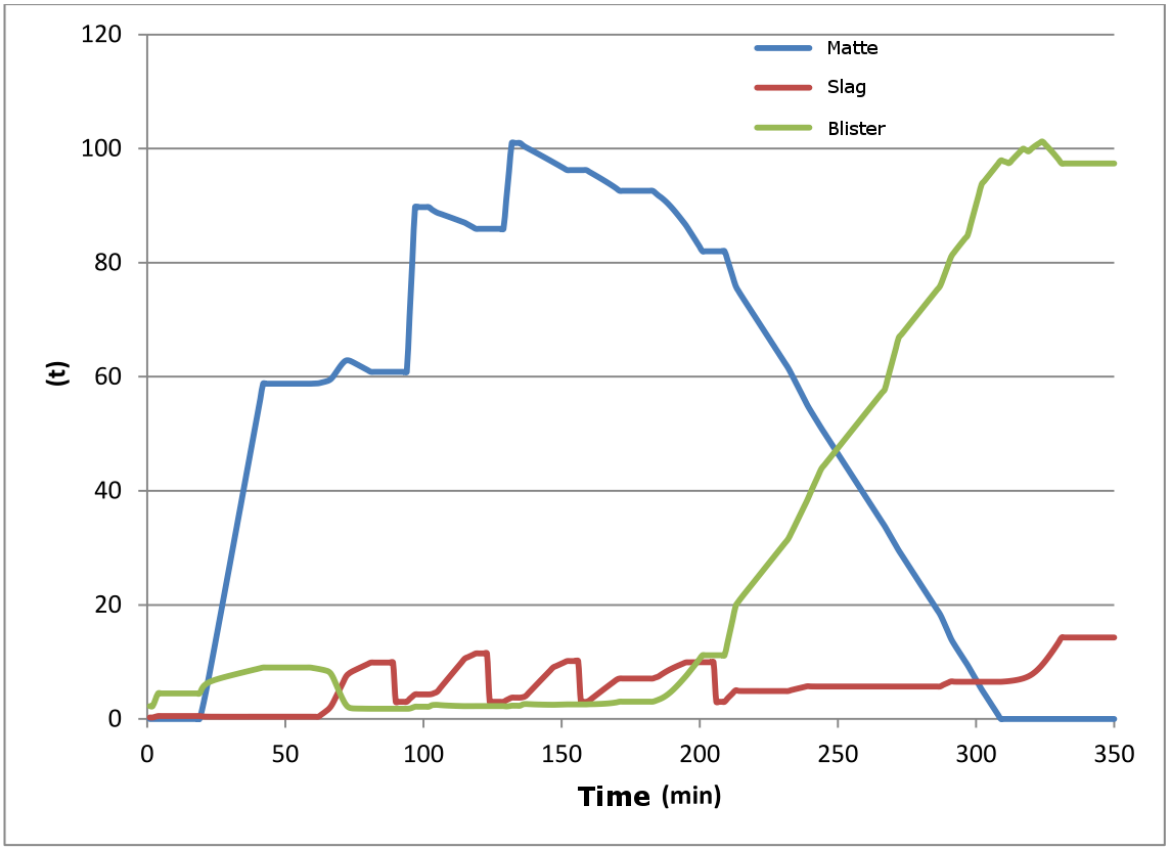


Figure 23. The formation of slag and blister at the expense of matte in the previous HSC PS converter models. [12]

5.7. Previous Matlab models

A similar Matlab model was implemented along with the SIMP project. The reactions in the Matlab model were defined through conditions and chemical formulas instead of chemical equilibrium. The input data was slightly modified in order to take residual matte and spills into account. The results from the Matlab model are shown in Figure 24.

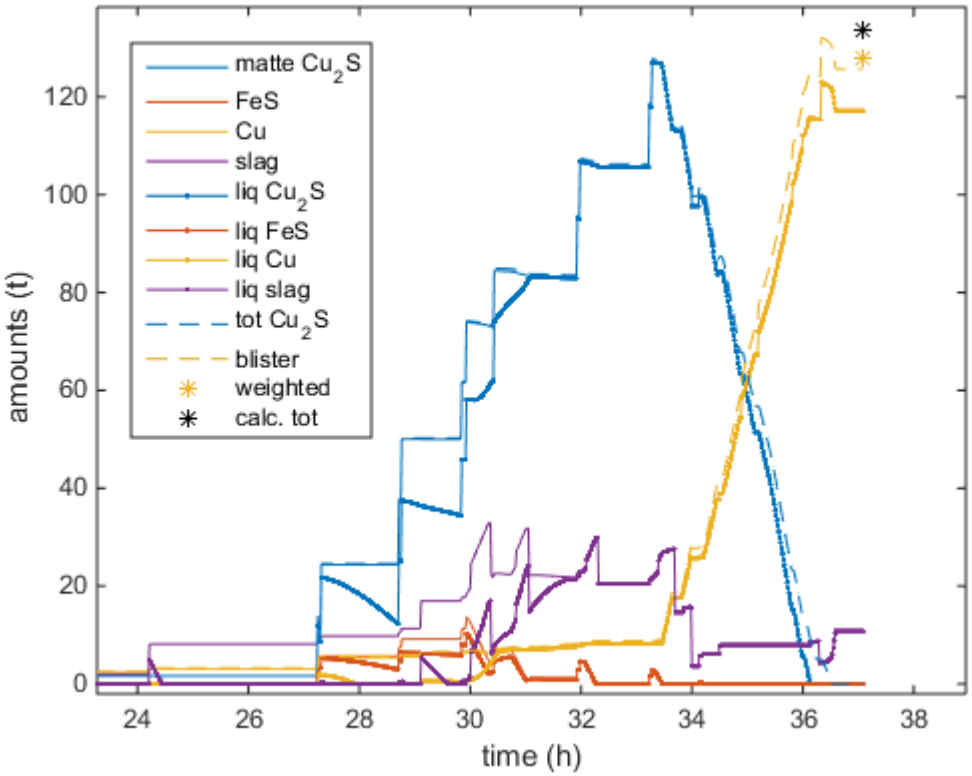


Figure 24. Quantities produced in previous Matlab models. [25]

The heat balance was implemented using the same formulas. The most notable difference in the Matlab model was that a shared temperature was used for the separate phases. The vessel was divided into five equal layers compared to three layers in the HSC model.

The heat loss calculations in the thesis model are based on those in Matlab, and the temperature behaviour should therefore be quite similar. However, comparing the temperatures in Figure 25 with the temperatures in the new model gives a temperature difference of about 75 °C. One hypothesis is that the use of fixed heat coefficients resulted in lower temperatures. Another possible explanation is that the reactions are implemented through formulas instead of chemical equilibrium, hence resulting in different outputs. The Matlab model was limited to only the primary elements and species, which may have had an impact on the temperature.

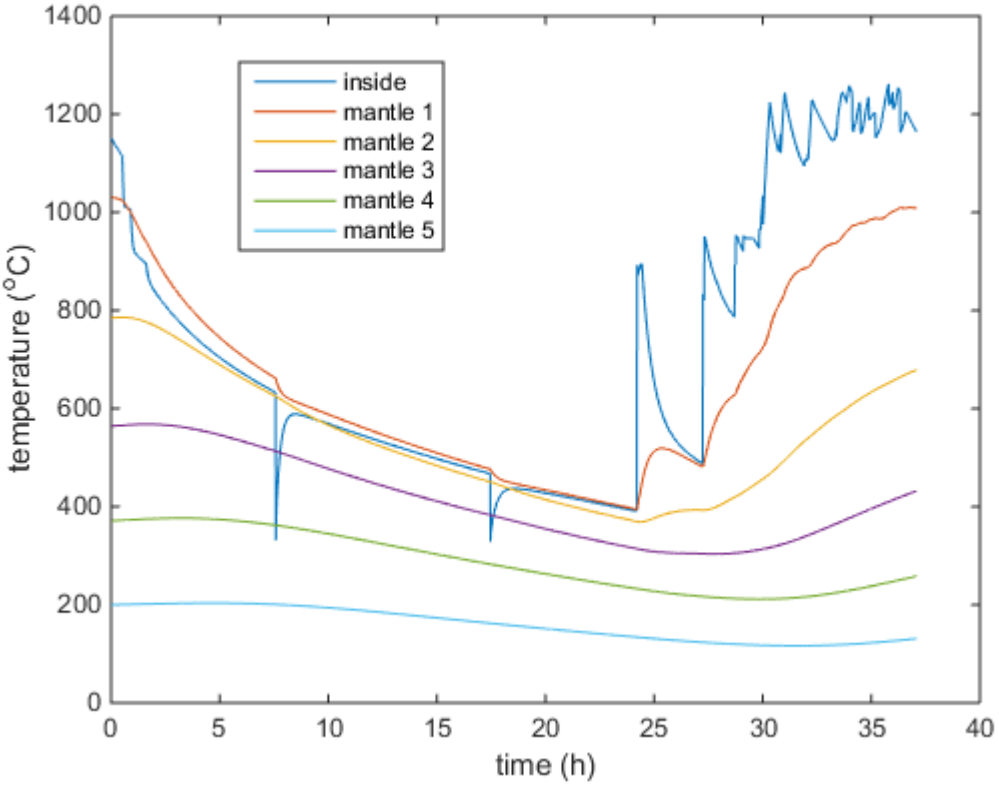


Figure 25. The temperature of the tank and layers in previous Matlab models. [25]

Comparing the model slag Cu % in Figure 26 with the Cu % in the new model gave quite similar results. The most notable difference is that the Cu % in the Matlab model is correctly increasing, as less iron is available, whereas the Cu % in the new model is more or less constant regardless of the available iron quantities. The difference in behaviour can be explained by the condition-based approach used in the Matlab model. The condition-based approach gives more accurate results, but is also harder to implement compared to the chemical equilibrium used in this thesis.

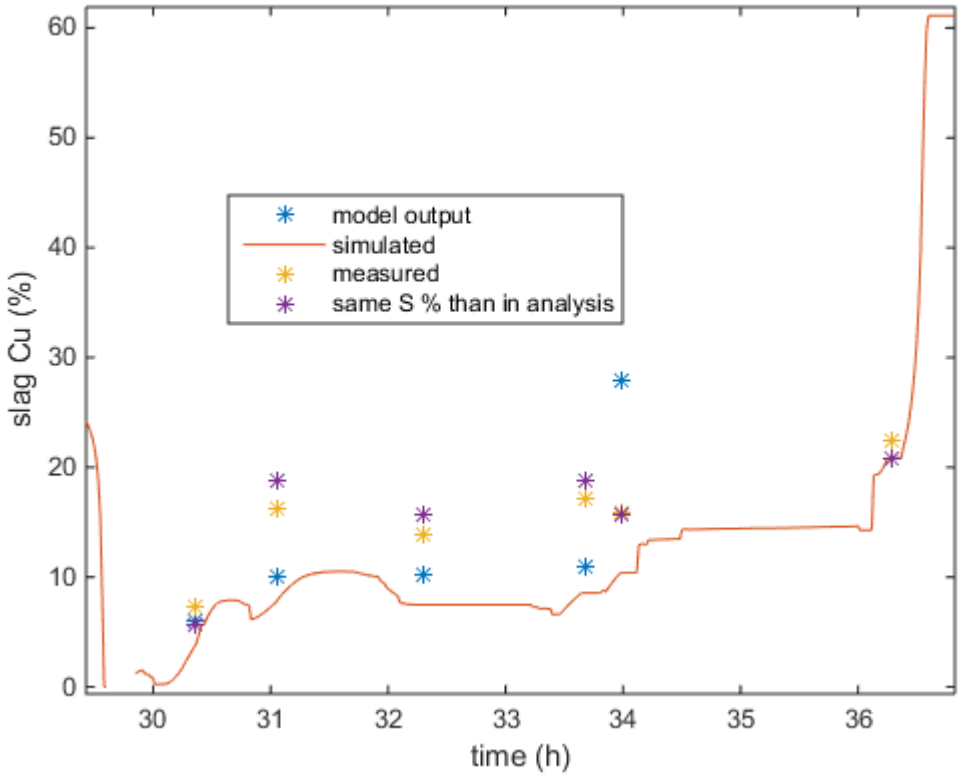


Figure 26. The Cu concentrate as well as the measured values in previous Matlab models. [25]

6. Conclusions

The target of this thesis was to develop a general calculation unit with dynamic features for the HSC Sim modelling platform. The calculation unit was designed as an easy-to-use basis for all types of thermal processes, with the purpose that it could be used as a template for more detailed process models. The new DLL-type calculation unit was tested and validated with a PS converter, which is one of the most complex batch reactors in the metal industry.

The design of the implemented unit was based on the steady-state pyrometallurgical HSC unit, although it also introduced some new concepts that were essential for dynamic simulation. The new unit comprised streams, tanks and operations. The content was conserved in tanks, which consisted of phases and species. Streams transferred content externally with the surroundings, whereas operations served as an interacting area between the different tanks.

The unit was programmed using a block-type structure where each block implemented a separate feature. The blocks could be divided into unit, model, data and view. Performance was a critical factor and optimized algorithms were therefore introduced in order to take the dynamic requirements into account.

A detailed PS converter was modelled on top of the new pyrometallurgical calculation unit. Slag, matte, blister and scrap metals were divided into different layers using tanks. The interacting area between layers was described through chemical equilibrium, and the rate at which content was transferred through the chemical equilibrium was proportional to the tank content. Heat was internally transferred through conduction between the layers, and externally through conduction over the vessel and radiation through the air vent.

The model was simulated based on data from a real-world smelter. The compositions and the temperatures were collected once a minute after each calculation step, and the data was analysed in order to obtain an overview of the process. The temperature profile indicated that the simulated operating temperatures were quite close to the corresponding literature data. Moreover, the conversion of matte to blister was quite similar to other PS converter models. The results were validated with two separate batches.

Full samples were taken from the simulation model at given intervals. The simulated samples were compared to the corresponding samples from the SIMP project. Overall, the PS model satisfies the requirements for a preliminary simulation model in terms of accuracy as the blister compositions were quite close to the sample data. The thesis did not include the fine-tuning of the model parameters, and the model still requires fixes and calibration in order to accurately model dust particles, impurities and the behaviour of slag.

The unit and the model will be further developed in other projects. The focus will be placed on modelling aspects, but the pyrometallurgical calculation unit may also undergo small improvements.

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Appendix 1 – The Simulation Schedule of the First Batch

Variable Name	Time	Mixed Revert Feed	Matte Feed	Revert and Scrap Feeds	Coke Feed	Silica Feed	Air Feed	Oxygen Content
Unit	(s)	t/h	t/h	t/h	t/h	t/h	Nm³/h	%
	60							
	120		120.9		24.6			
	180		0		0			
	35700			132				
	35760			0				
	60000			84				
	60300			0				
	70200							
	70860		237					
	71100		255					
	71340		0					
	76140		334					
	76320		312					
	76500		0					
	77640			78				
	77940			0				
	80220		183.6					
	80520		195.6					
	80580						22300	22
	80820		0			137.3	32000	26.8
	80940					0		
	82140						0	21
	82320		232.5					
	82560		0					
	83460						30600	21.1
	83760					84.63	31500	26.1
	83880					0		
	84640						0	21
	87720		312					
	87900		298					
	88080		0					
	88200						26600	21
	88320					41.76	31700	24.3
	88500					0	33700	26.3
	89040						0	21
	92400		308					
	92580		224					
	92760		0				24900	
	93000					52.74	33000	26.3

	93180				0		
	94020					0	21
	94560					31900	23.1
	94620				20.88		
	94800				0	33500	26.1
	95220					0	21
	95700	94					
	95880	0				30500	
	96240					34000	24.4
	96900					0	21
	97020		78				
	97200		0			32600	21.5
	97500					33000	25
	98400		84			12200	21
	98580		0			32300	
	99420					12800	
	99480		94				
	99660		0				
	99720					29800	
	100380					30940	24.4
	101700		76				
	101880		0				
	102420		87			27100	23.5
	102540		0				
	103380					0	21
	103560		117				
	103680					30100	
	103800		0				
	104600					0	

Variable Name	Time	Slag Max	T Vessel In	T Vessel Mid	T Vessel Out	Vent Is Open
Unit	(s)	kg	°C	°C	°C	TRUE/FALSE
	60	1000000	1000	500	220	0
	70320					1
	71340					0
	76140					1
	76500					0
	77640					1
	77940					0
	80220					1
	80820					0
	82140	6000				1
	82200	1000000				
	82560					0
	83760					1
	83880					0
	84600	5000				1
	84660	1000000				0
	87720					1
	88080					0
	88320					1
	88500					0
	89100	4000				1
	89160	1000000				0
	92400					1
	92760					0
	93000					1
	93180					0
	94080	3000				1
	94140	1000000				0
	94620					1
	94800					0
	95340	3000				1
	95400	1000000				0